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(54) Title: HIGH DENSITY VISCOSIFIED AQUEOUS COMPOSITIONS

(57) Abstract

Advantageous aqueous mixed salt systems viscosified with water-soluble or water-dispersable polymers which are superior to corresponding single salt systems of similar densities are provided. The mixed salt systems comprise water; a water-soluble or water-dispersable polymer capable of viscosifying an aqueous medium; one or more cations including a member selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and one or more anions including a member selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion or mixtures thereof; there being present either at least two cations or at least two anions. Inventive viscosified mixed salt systems display - under such stressing factors as aging, heat, mechanical agitation, and shear - greater stability compared to the single salt systems of similar densities. Also provided are methods for making viscosified mixed salt systems and methods for advantageously using the same as drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids.

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## HIGH DENSITY VISCOOSIFIED AQUEOUS COMPOSITIONS

### REFERENCE TO RELATED APPLICATIONS

This application claims priority upon U.S. Patent Application Serial No. 5 60/010,051 filed January 16, 1996, which is hereby incorporated by reference in its entirety.

### BACKGROUND OF THE INVENTION

#### Field of the Invention

The present invention relates generally to the exploitation of 10 subterranean formations. More specifically, it relates to the exploitation of subterranean petroliferous formations using high density mixed-brine-based fluids such as drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids. Yet more 15 specifically, the field of this invention is fluid rheology, thickeners, viscosifiers, viscoelastic fluids, and the physical hydration of polymer additives into high density mixed-brine-based drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids.

#### Discussion of Related Art

A wide variety of methods for exploiting subterranean petroliferous 20 formations are known in the art, and the problems associated therewith are also well known. Brines are commonly used in drilling, drill-in, work-over, hydraulic fracturing, completion, packer, well treating, testing, spacer, or hole abandonment fluids because of their wide density range and their character of being free of suspended solids and essentially non-damaging to subterranean 25 petroliferous formations. During the process of drilling and completing an oil

well, it is often desirable to add polymer and possibly bridging agents, to viscosify the drilling or completion fluid and thereby to control fluid loss to the formation. As fluids are lost into the formation, these materials filter out and build up a filter cake at the rock face which limits further flow of fluids into the formation. Some fluids nevertheless invariably flow into the formation and can interact with formation matrix in such a way as to reduce the permeability of the formation to the subsequent in-flow or out-flow of fluid, especially oil, gas, condensate or other fluid targeted for withdraw and use. This reduction in the rock permeability is termed "formation damage".

Xanthan gum is commonly used as a viscosifying polymer in brine-based drilling fluids whereas the cheaper hydroxyethyl cellulose (HEC) is commonly used in a work-over fluid. Xanthan gum has superior tolerance to high pH and temperature and has superior thixotropic properties compared to other viscosifying polymers. The viscosifying polymer is usually added to the brine to thicken it so that it will have, for example, high carrying capacity for the cuttings produced while drilling and high viscosity for a work-over fluid to control fluid loss and minimize formation damage. Xanthan gum also has the ability to impart gel character to a brine so that it will have high carrying capacity for drill cuttings even when the drilling process is interrupted and the fluid becomes quiescent.

HEC is a typical viscosifier and fluid loss control agent which is known to cause relatively little damage to the formation. Guar gum and starch derivatives can also be used. However, HEC and other polymers are very slow to viscosify brines having densities above about 12.0 ppg and HEC does not viscosify formate brines. Heating can be required to reach a desired viscosity for some brines.

For many applications of brine-based drilling fluids, HEC lacks sufficient thermal stability and carrying capacity for the drill cuttings. In these cases,

therefore, xanthan gum is typically used instead. While such agents as HEC and xanthan gum impart both viscosity and fluid loss control to the drilling, drill in, completion, hydraulic fracturing, work over, well treating, spacer, or hole abandonment fluids, starches are often added to augment the fluid loss properties. Standard brine based drilling fluid may also include a bridging agent, such as, for example, sized particles of calcium carbonate or sodium chloride. In addition, a representative brine based drilling fluid can also include, for example, corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, and/or weighting agents.

Conventional techniques for viscosifying a brine are limited by the fact that so much of the water in the brine is devoted to solubilization of the salt that there is not enough water left over for the solubilization of the viscosifying agent. In effect, the viscosifying agent is "salted out". Additionally, mixed-salt brines are often limited by salt solubilities to relatively low densities. For example, when a dense brine based on NaBr is added to a dense brine based on Ca(NO<sub>3</sub>)<sub>2</sub>, the precipitation of solid NaNO<sub>3</sub> depletes the solution so much that the remaining brine is only of relatively moderate density. As another example, the same sort of interaction and precipitation occurs when a dense brine based on CaCl<sub>2</sub> or CaBr<sub>2</sub> is added to a dense brine based on K<sub>2</sub>CO<sub>3</sub>. The present invention teaches a group of mixed salts which are preferred because they can be formulated up to relatively high densities and yet the availability of "free" water is sufficient to allow viscosifying polymers to hydrate acceptably up to relatively high concentrations. Hence, inventive mixed-salt compositions are capable of exhibiting relatively high viscosities.

Problems occur when attempting to use xanthan gum to viscosify high concentrations of divalent-cation-based brines where most of the water is associated with salt. These problems include the need for extended mixing times, high shear, and/or heat in order to viscosify the brine. Similar problems

occur with other viscosifiers. These problems are relatively minor in the brine concentration range extending most of the way from fresh water to almost saturated brine, then suddenly the problems get much more serious when just a relatively small amount of extra salt is added to a near-saturated brine.

One example is viscosifying xanthan gum in brines having high concentrations of  $\text{CaBr}_2$ , where most of the water is occupied by the salt. This system requires extended mixing times, high shear, and/or heat in order to viscosify the brine. (See Table 1A).

TABLE 1A

	wt. % CaBr <sub>2</sub>	% saturation	Base Brine Density (ppg)	Steps Needed to Viscosify the Brine Uniformly @ 1 - 5 ppb
5	0 to 47.9	0.0 to 83.5	8.3 to 13.5	Stirring xanthan gum into the brine at room temperature; no extra shear needed; no extra heating needed.
	48.5 to 51.3	84.5 to 89.4	13.6 to 14.1	Stirring xanthan gum into the brine at room temperature followed by moderate shearing or mild warming.
10	51.9	90.4	14.2	Stirring xanthan gum into the brine followed by extensive shearing at room temperature or mild shearing combined with moderate heating.
15	52.4 to 57.4	91.3 to 100.0	14.3 to 15.35	Stirring xanthan gum into the brine at room temperature followed by extensive mixing and shearing while heating steadily until polymer hydrates sufficiently.

The data clearly show the need for extended mixing times, high shear, and/or heat in order to viscosify CaBr<sub>2</sub> brines above about 85% saturation.

When 3 pounds per barrel (ppb) of xanthan gum is added to a 14.2 pounds per gallon (ppg) substantially pure CaBr<sub>2</sub> solution, stirred vigorously for an hour at room temperature, 70°F, and sheared for 10 minutes on a Silverson mixer Model L4RT at 4000 rpm, it does not viscosify by indication of a yield point (YP) of 0 measured on a variable speed rheometer. It was noticed that by stirring the solution energetically for one hour at 125°F the xanthan gum viscosified with a YP of 62 and a viscosity at the 3 rpm reading of 2700 cp as shown in Table 1B. Stirring shears the solution but not nearly the amount of shear the Silverson mixer can provide.

To determine the temperature at a specific shear needed to viscosify 14.2 ppg CaBr<sub>2</sub> solutions, a Fann Model 50 study was performed to monitor the viscosity at shear and temperature with time. The solutions were slowly heated to 150°F at 0.5 degrees per minute and allowed to remain at that temperature until maximum viscosity was achieved. Two separate tests were performed at shear rates of 511 sec<sup>-1</sup> (300 rpm) and 170 sec<sup>-1</sup> (100 rpm). The temperatures at which 25% of maximum viscosity was obtained were found to be 122°F and 143°F, respectively. FIG. 1 illustrates these results and shows that 2.5 additional hours are needed to viscosify the solution at 170 sec<sup>-1</sup> (100 rpm) than at 511 sec<sup>-1</sup> (300 rpm). Table 1B below also shows the maximum viscosity of this 14.2 ppg CaBr<sub>2</sub> solution obtained by different methods. This indicates that heating and shearing equipment would be needed in order to fully viscosify this solution.

**TABLE 1B****14.2 ppg CaBr<sub>2</sub> + 3 ppb of Xanthan**

RPM	Viscosity, cp 70°F	Viscosity, cp 70°F	Viscosity, cp 70°F	Viscosity, cp 70°F
5	600	11	78	81
	300	11	109	109
	3		2700	2600
	PV	11	47	53
	YP	0	62	56
	n		0.32	0.33
	K, cp		7000	6700
	Method	Stirred 1 hour at 70°F, shear 10 min/4000rpm	Stirred energetically for 1 hour at 125°F	Fann Model 50 at 170 sec <sup>-1</sup> at 150°F for 5 hrs.
				Fann Model 50 at 511 sec <sup>-1</sup> at 150°F for 2 hrs.

15 It has been shown that biopolymers like xanthan gum show a transition temperature ( $T_m$ ) in brines of various densities. A transition temperature is the temperature at which the polymer undergoes an order-disorder conformation change. This conformation change is accompanied by a massive loss of viscosity and increase in the rate of hydrolytic degradation by two orders of magnitude. It has also been shown that CaBr<sub>2</sub> solutions above 10.4 ppg have a  $T_m$  of less than 80°C and that degradation occurs at higher densities.  $T_m$  has been used as a guide for predicting thermal stability of the polymers in brine solutions.

20 A variety of well servicing fluids and associated systems have been proposed in the prior art. There has remained a need for improved systems having advantageous characteristics for viscosification and fluid loss control,

dispersability and hydration. Accordingly, the present invention is directed toward enhancing the thermal stability, viscosity and gel structure of dense brine-based drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids and toward increasing the thermal stability of the water-soluble or water-dispersable polymer used to viscosify and gel the brines.

## SUMMARY OF THE INVENTION

According to the present invention, there are provided mixed salt compositions that are viscosified easily and have superior stability compared to a corresponding single salt composition having a similar density. For example, 5 the present inventors have discovered that a 14.2 ppg  $\text{CaBr}_2$  and  $\text{CaCl}_2$  mixture is extremely difficult or impossible to fully viscosify with xanthan gum or other viscosifiers without introducing significant heat and shear; however, if a 13.6 ppg  $\text{CaBr}_2$  solution is weighted with dry  $\text{NaBr}$  to 14.2 ppg it is relatively easier to viscosify without the introduction of significant shear or heat. The present 10 inventors have also discovered, for example, that the stability of biopolymers in a calcium-based brine is dramatically improved when the formulation of the base brine is optimized with respect to the calcium chloride and calcium bromide content.

According to the present invention there are provided high-density, 15 viscosified, aqueous compositions having superior stability under stress factors such as aging, heat, mechanical agitation and shear. Inventive compositions comprise water; a water-soluble or water-dispersable polymer; one or more cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and one or more anion selected from the group consisting of chloride, bromide, iodide, formate, 20 nitrate, acetate, cyanate, thiocyanate, a zinc complex anion, or mixtures thereof; wherein there are present either at least two cations or at least two anions in effective amounts to provide advantageous stability. In alternate preferred aspects of the invention, inventive compositions have superior heat stability, 25 exhibited by a  $\tau_{50}$  of at least about 1; superior shear stability, exhibited either by a  $\zeta_{50}$  of at least about 1 or by a  $\omega_{50}$  of at least about 1; superior fluid loss control, exhibited by a  $\psi_{50}$  of at most about 1; or superior pH stability, exhibited by a  $\phi$  of at least about 1.

Also provided by the present invention are methods for making high-density, viscosified, aqueous compositions having superior stability under stress factors. In a preferred aspect of the invention, the method comprises providing an aqueous solution comprising a first amount of one or more cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof  
5 and a second amount of one or more anion selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion, or mixtures thereof, wherein there are present either at least two cations or at least two anions in effective amounts to provide the  
10 advantageous viscosification stability; and mixing a water-soluble or water dispersable polymer into the solution to yield a final composition having a  $\tau_{50}$  of at least about 1; a  $\zeta_{50}$  of at least about 1; a  $\omega_{50}$  of at least about 1; a  $\psi_{50}$  of at most about 1; or a  $\phi$  of at least about 1. Preferably, the aqueous solution is  
15 prepared by dissolving into water at least two salts, as described herein, to provide a salt solution having a density of greater than about 9.5 pounds per gallon (ppg). Additionally provided are methods for using inventive high-density, viscosified, aqueous compositions including using the compositions as  
drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well  
20 treating, testing, spacer, or hole abandonment fluids.

It is an object of the present invention to provide mixed salt systems that are viscosified easily compared to a single salt system having similar density.

Additionally, it is an object of the present invention to provide a viscosified mixed salt system that displays greater stability under such stressing factors as aging, heat, mechanical agitation, and shear, compared to the single salt system  
25 of similar density.

Another object of the present invention is to provide high density mixed-salt brines having more stable rheological properties, especially at elevated

temperatures and over extended periods of time, and which rheological properties are more resistant to heat- and shear-degradation.

It is also an object of the invention to provide viscosified high density mixed-salt brines having low crystallization temperatures and broad ranging compatibility with, for example, fluid-loss agents, sea water, formation water and spacers.

Additional objects, features and advantages will be apparent from the following description.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**FIG. 1** is a plot of viscosity and temperature versus time and displays the temperature at a specific shear needed to viscosify 14.2 ppg  $\text{CaBr}_2$  solutions.

**FIG. 2** is a plot of percent viscosity versus temperature for two single salt systems and one mixed salt system.

**FIG. 3** is a plot of  $T_{50}$  ( $^{\circ}\text{F}$ ) versus percent  $\text{CaBr}_2$  in a 10.5 ppg  $\text{CaCl}_2/\text{CaBr}_2$  solution.

**FIG. 4** is a plot of percent viscosity versus temperature, showing viscosity data and the  $T_m$  for 12.5 ppg  $\text{NaBr}$  and mixtures of 13.0 ppg  $\text{CaBr}_2/\text{NaBr}$  and showing viscosity data for pure  $\text{CaBr}_2$ .

**FIG. 5** is a plot of  $T_{50}$  ( $^{\circ}\text{F}$ ) versus pounds of  $\text{NaBr}$  per barrel for a 13 ppg  $\text{CaBr}_2/\text{NaBr}$  solution.

**FIG. 6** is a plot of percent viscosity versus temperature for a test of thermal stability of pre-gelatinized starch as described more fully in Example 5.

**FIG. 7** is a plot of  $T_{50}$  ( $^{\circ}\text{F}$ ) versus pounds of  $\text{LiBr}$  per barrel for a 12.5 ppg  $\text{NaBr}/\text{LiBr}$  solution.

**FIG. 8** is a plot of  $T_{50}$  ( $^{\circ}\text{F}$ ) versus pounds of  $\text{LiBr}$  per barrel for a 13 ppg  $\text{CaBr}_2/\text{LiBr}$  solution.

**FIG. 9** is a plot of  $T_m$  ( $^{\circ}\text{F}$ ) versus percent 11.0 ppg  $\text{NaNO}_3$  brine in 11.0 ppg  $\text{NaHCO}_3/\text{NaNO}_3$  brine mixtures.

**FIG. 10** is a plot of Yield Point (YP) versus pounds  $\text{MgCl}_2$  in a 10.5 ppg  $\text{CaCl}_2/\text{MgCl}_2$  solution.

**FIG. 11** is a plot of pH versus the log of the molar ratio of total halides to zinc, and is described in greater detail in Example 16.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the invention, and such further applications of the principles of the invention as described therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

The present invention provides high density, viscosified, aqueous compositions having superior stability under stress factors such as aging, heat, mechanical agitation and shear. To advantageously practice the present invention, starting materials include at least two different salts, each comprising a cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and an anion selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion, or mixtures thereof. Salts advantageously used in accordance with the present invention are readily available commercially.

In one preferred composition according to the invention, there are present a cation having a +2 charge and a cation having a +1 charge. In an alternate preferred aspect of the invention the first cation and the second cation each have a +2 charge. In another preferred aspect of the invention, the composition comprises a chloride anion and a bromide anion. Examples of preferred salt combinations useful for preparing inventive compositions include the following:

lithium chloride/lithium bromide  
calcium chloride/calcium bromide

sodium bromide/calcium bromide  
lithium bromide/sodium bromide  
lithium bromide/calcium bromide  
sodium chloride/potassium chloride  
5 sodium chloride/calcium bromide  
sodium chloride/sodium bromide  
sodium bromide/potassium bromide  
sodium formate/sodium nitrate  
sodium formate/potassium nitrate  
10 potassium formate/sodium nitrate  
sodium formate/cesium nitrate  
cesium formate/sodium nitrate  
potassium formate/cesium nitrate  
sodium formate/potassium nitrate  
15 lithium formate/cesium nitrate  
cesium formate/lithium nitrate  
potassium formate/calcium nitrate  
calcium formate/potassium nitrate  
potassium formate/potassium nitrate  
20 cesium formate/cesium nitrate  
potassium chloride/potassium bromide  
potassium bromide/calcium bromide  
potassium chloride/calcium bromide  
potassium formate/ calcium bromide  
25 magnesium chloride/calcium chloride  
magnesium chloride/calcium bromide  
magnesium bromide/calcium bromide  
magnesium chloride/magnesium bromide  
cesium chloride/cesium bromide  
30 cesium chloride/sodium chloride  
cesium bromide/sodium chloride  
cesium chloride/sodium bromide  
cesium bromide/sodium bromide  
cesium chloride/potassium chloride  
35 cesium bromide/potassium chloride  
cesium chloride/potassium bromide  
cesium bromide/potassium bromide  
cesium chloride/calcium chloride  
cesium bromide/calcium chloride  
cesium chloride/calcium bromide  
40 cesium bromide/calcium bromide

calcium chloride/calcium formate  
calcium bromide/calcium nitrate  
calcium bromide/cesium bromide  
zinc complex salts/alkali metal or alkaline earth metal salts

5 More detailed descriptions of various selected compositions prepared in accordance with the present invention appear below in the Examples. It should be noted that in inventive compositions, the salts are substantially dissolved into water. As such, a statement that a particular inventive composition includes two salts is intended to mean that the composition includes the cations and anions of the salt, although these cations and anions may be, for example, 10 in the ionic state or complexed with other ions or materials.

It is also contemplated by the present invention that preferred compositions may be prepared using as starting materials three or more different salts. In this regard, in one preferred aspect, inventive compositions comprise three different 15 cations, a first cation having a +2 charge, a second cation having a +2 charge, or a second cation in which the cation is held as a complex having cationic, neutral, or anionic form, and a third cation having a +1 charge.

Another starting material for the practice of the invention is a water-soluble or water-dispersable polymer. Preferably the polymer used in accordance with 20 the present invention is a biopolymer, and is more preferably selected from the group consisting of algin; anionic cellulose; anionic polysaccharide; cationic polysaccharide; carboxymethyl cellulose; carboxymethyl hydroxyethyl cellulose; gellan gum; guar gum; gum ghatti; gum karaya; gum tragacanth; gum arabic; gum acacia; locust bean gum; methacrylic acid polymer; polyamine; 25 polyanionic cellulose; iota, lambda or kappa sulfated polysaccharides; polysaccharides modified by i) cross-linking, ii) hydroxyethylation, iii) hydroxypropylation, iv) carboxymethyl-hydroxyethylation, v) carboxymethyl-hydroxypropylation, vi) carboxymethylation, or vii) carboxylation; rhamsan

gum; vinyl compound polymer; wellan gum or glycol-compatible wellan gum; xanthan or xanthan gum; or mixtures of said polymers. More preferably, the polymer is selected from the group consisting of anionic polysaccharide; cationic polysaccharide; gellan gum; guar gum; rhamsan gum; wellan gum; xanthan or xanthan gum or modifications of said polymers by I) cross-linking, ii) hydroxyethylation, iii) hydroxypropylation, iv) carboxymethyl-hydroxyethylation, v) carboxymethyl-hydroxypropylation, vi)carboxymethylation, or vii) carboxylation; or mixtures of said polymers. It is readily understood that additional polymers having thixotropic properties or gel structure properties similar to those specifically mentioned may also be advantageously used in accordance with the present invention. Polymers useful according to the present invention are readily available commercially.

Inventive compositions are, generally, dense salt solutions viscosified with a polymer. Inventive compositions comprise water; a water-soluble or water-dispersable polymer; one or more cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and one or more anion selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion or mixtures thereof; wherein there are present either at least two cations or at least two anions in effective amounts to impart to the composition advantageous stability under stressing factors such as heat, shear and pH.

Inventive compositions are preferably prepared from the following starting materials in the proportions given: from about 10.0 to about 90.0 weight percent water; from about 0.01 to about 45.0 weight percent polymer; from about 0.05 to about 85.0 weight percent of a first salt; and from about 0.05 to about 85.0 weight percent of a second salt. In an alternate preferred embodiment, also added is from about 0.05 to about 85.0 weight percent of a third salt. More preferably, inventive compositions are prepared using the

following proportions of starting materials: from about 0.5 to about 10 weight percent polymer; from about 2 to about 80 weight percent of a first salt; and from about 2 to about 40 weight percent of a second salt and optionally from about 2 to about 80 percent of a third salt. Additionally, the relative amounts of each salt may advantageously be optimized with minimal experimentation to accomplish the desired results described herein.

It is readily understood by one of ordinary skill in the art that additional materials may also be included in preferred compositions. Examples of such additives include starch, bridging agents (such as, for example, sized particles of calcium carbonate or sodium chloride), corrosion inhibitors, lubricants, pH control additives, surfactants and/or weighting agents.

In another aspect of the invention, high-density, viscous compositions are made by first providing an aqueous solution having dissolved therein at least one cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof, and at least one anion selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion, or mixtures thereof, wherein there is present either at least two cations or at least two anions in amounts effective to achieve the desired stability; and then mixing a water-soluble or water-dispersable polymer into the brine. The aqueous solution may be provided, for example, by dissolving into water a first salt and a second salt, each comprising a cation selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and an anion selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion, or mixtures thereof. Preferably the resulting salt solution has a density of greater than about 9.5 pounds per gallon (ppg), more preferably greater than about 10 ppg, and yet more preferably greater than about 11.5 ppg.

Alternatively, the polymer is added to a brine, having dissolved therein one salt, before adding the second salt either in the form of a brine or a solid salt. The resulting composition in either instance preferably includes at least about 0.1 pounds per barrel (ppb) of the polymer, at least about 1% cations by weight, 5 and at least about 1% anions by weight; more preferably at least about 0.2 ppb polymer, at least about 5% cations by weight, and at least about 5% anions by weight; and most preferably at least about 0.4 ppb polymer, at least about 10% cations by weight, and at least about 10% anions by weight.

Depending upon the specific salt composition of a given system, the 10 addition of the polymer may be facilitated by heating the mixture while stirring. An advantageous feature of the invention, however, is the relative ease with which polymers may be hydrated by relatively dense salt solutions. This feature is described in greater detail below in the Examples with regard to various selected inventive compositions. In one preferred aspect of the 15 invention, the polymer is mixed into the brine by first hydrating, solvating or swelling the polymer at least partially in a fluid medium, and then mixing the fluid medium with the brine.

Compositions of the present invention exhibit superior stability under such 20 stressing factors as aging, heat, mechanical agitation and shear, this feature being very important in fluids utilized in the field of subterranean drilling. The term "stability" as used herein is intended to refer to the ability of an inventive composition to withstand various stress conditions before the viscosifying polymer's capability to viscosifying the fluid composition is substantially diminished. By "substantially diminished" it is meant diminished to an extent 25 where the composition may no longer be advantageously used for its intended purpose. Diminished viscosity is commonly referred to in the relevant trade as fluid degradation.

A technique used to measure relative heat stability involves a determination of  $\tau_{50}$  of a mixed salt/polymer composition. To determine  $\tau_{50}$  of an inventive composition,  $T_{50}$  of a mixed salt composition is determined and related to the  $T_{50}$  of one or more of the related single salt systems according to the following equation:

$$\tau_{50} = \frac{2 * T_{50}(A/B)}{T_{50}(A) + T_{50}(B)}$$

wherein (A/B) indicates that the preceding value is a property of the two salt system; (A) represents a corresponding single salt system; and (B) represents the other corresponding single salt system. The term "corresponding single salt system" as used herein is intended to designate a composition consisting essentially of only cations and anions derived from one salt, this salt being one of the salts dissolved in the preparation of the particular inventive two or three salt composition.  $T_{50}$  of a composition is determined by heating the composition at a given rate and recording the temperature at which the viscosity of the composition is half of its viscosity at room temperature. In one aspect of the invention, inventive two salt systems exhibit a  $\tau_{50}$  of greater than about 1. This means that the  $T_{50}$  of the inventive two salt system is greater than expected based upon the linear relationship between  $T_{50}$  values for the two corresponding single salt systems. As such, there are two corresponding single salt systems for each inventive two salt system. Table 1C shows  $\tau_{50}$  computations for various systems according to the present invention.

**Table 1C**  
 **$\tau_{50}$  of Various Mixed Salt Systems**

	Density (ppg)	Mixed Salt System A/B	$\tau_{50} =$ $\frac{2 \times T_{50}(A/B)}{T_{50}(A) + T_{50}(B)}$	$T_{50}(A/B)$ (F°)	$T_{50}(A)$ (F°)	$T_{50}(B)$ (F°)
5	12.5	LiBr/NaBr (50/50)	1.084	219.5	114	291
	12.5	LiBr/NaBr (25/75)	1.296	262.5	114	291
	13.0	LiBr/CaBr <sub>2</sub>	1.780	266	114	184.8
10	9.0	NaCl/NaBr	>1.0	300	300	>291
	10.5	NaCl/NaHCO <sub>3</sub>	1.173	352	300	300
	9.0	NaCl/KCl	1.000	300	300	300
15	10.5	MgCl <sub>2</sub> /CaBr <sub>2</sub> (35.6/64.4)	1.041	255	268	222
	10.5	CaCl <sub>2</sub> /CaBr <sub>2</sub>	1.117	257	238	222
	12.5	NaBr/KHCO <sub>3</sub>	0.842	294	290.7	408
20	10.5	MgCl <sub>2</sub> /CaCl <sub>2</sub>	0.949	240	268	238
	10.5	MgCl <sub>2</sub> /CaBr <sub>2</sub> (50/50)	0.992	243	268	222
	10.5	MgCl <sub>2</sub> /CaBr <sub>2</sub> (45/55)	0.988	242	268	222
	10.5	MgCl <sub>2</sub> /CaBr <sub>2</sub> (30/70)	0.986	241.6	268	222

Density (ppg)	Mixed Salt System A/B	$\tau_{50} = \frac{2 \times T_{50}(A/B)}{T_{50}(A) + T_{50}(B)}$	$T_{50}$ (A/B) (F°)	$T_{50}$ (A) (F°)	$T_{50}$ (B) (F°)
10.5	MgCl <sub>2</sub> /CaBr <sub>2</sub> (25/75)	0.967	237	268	222
5	CaBr <sub>2</sub> /Ca(NO <sub>3</sub> ) <sub>2</sub>	0.935	202.5	184.8	248.3

Although various systems have  $\tau_{50}$  values slightly less than 1, these systems have improved characteristics according to various other aspects of the invention, such as, for example, improved shear stability, improved pH stability and/or improved ability to control fluid loss into a formation.

10 Another important feature of fluids utilized in the subterranean drilling industry is shear stability or stability under shear stress. The term "shear" is intended to refer to the ratio between a stress (force per unit area) applied laterally to a material and the strain resulting from this force. Determination of this ratio is one method of measuring the viscosity of a liquid or semisolid.

15 One manner of measuring shear stability involves a determination of  $\zeta_{50}$ . To determine  $\zeta_{50}$  of an inventive composition,  $\xi_{50}$  of a mixed salt composition is determined and related to the  $\xi_{50}$  of one or more of the related single salt systems according to the following equation:

$$\zeta_{50} = \frac{2 * \xi_{50}(A/B)}{\xi_{50}(A) + \xi_{50}(B)}$$

20  $\xi_{50}$  represents the time, in an experiment conducted at no greater than  $T_{50}$ , at which sustained shear degradation at a shear stress rate of at least 1021 sec<sup>-1</sup> causes the mixture viscosity to drop to 50% of its initial value at that same temperature ( $T_{50}$ ). The viscosity is measured at both initial and final conditions

at a shear stress rate of 170 sec<sup>-1</sup>. In one aspect of the invention, inventive two salt systems exhibit a  $\zeta_{50}$  of greater than about 1. This means that the  $\xi_{50}$  of the inventive two salt system is greater than expected based upon the linear relationship between the  $\xi_{50}$  values for the two corresponding single salt systems. As before, there are two corresponding single salt systems for each inventive two salt system.

Another manner of measuring shear stability involves a determination of  $\omega_{50}$ . To determine  $\omega_{50}$  of an inventive composition,  $\sigma_{50}$  of a mixed salt composition is determined and related to the  $\sigma_{50}$  of one or more of the related single salt systems according to the following equation:

$$\omega_{50} = \frac{2 * \sigma_{50}(A/B)}{\sigma_{50}(A) + \sigma_{50}(B)}$$

$\sigma_{50}$  represents the shear rate, in an experiment conducted at a temperature no greater than  $T_{50}$ , at which sustained shear degradation for at least 30 minutes causes the mixture viscosity to drop to 50% of its initial value at that same temperature ( $T_{50}$ ). The viscosity is measured at both initial and final conditions at a shear stress rate of 170 sec<sup>-1</sup>. In one aspect of the invention, inventive two salt systems exhibit a  $\omega_{50}$  of greater than about 1. This means that the  $\sigma_{50}$  of the inventive two salt system is greater than expected based upon the linear relationship between the  $\sigma_{50}$  values for the two corresponding single salt systems.

Another important feature of fluids utilized in the subterranean drilling industry is fluid loss control. The term "fluid loss" is intended to refer to the leak-off of fluid into the rock matrix. One manner of measuring fluid loss control involves a determination of  $\psi_{50}$ . To determine  $\psi_{50}$  of an inventive composition,  $\rho_{50}$  of a mixed salt composition is determined and related to the

$\rho_{50}$  of one or more of the related single salt systems according to the following equation:

$$\psi_{50} = \frac{2 * \rho_{50}(A/B)}{\rho_{50}(A) + \rho_{50}(B)}$$

$\rho_{50}$  represents the ratio of the API standard fluid loss volume, in an experiment conducted at a temperature no greater than  $T_{50}$  after 16 hours of rolling heat aging at a temperature no greater than  $T_{50}$ . In one aspect of the invention, inventive two salt systems exhibit a  $\psi_{50}$  of less than about 1. This means that the  $\rho_{50}$  of the inventive two salt system is less than expected based upon the linear relationship between the  $\rho_{50}$  values for the two corresponding single salt systems. As before, there are two corresponding single salt systems for each inventive two salt system.

Another important feature of fluids utilized in the subterranean drilling industry is pH stability. It is widely known to those skilled in the art that such processes as acid- or base- catalyzed hydrolytic degradation can lead to loss of viscosifying capability on the part of the polymer. Accordingly, the process of formulating a viscosified fluid involves searching for a pH range wherein these chemical degradation processes are held to acceptable rates and then maintaining the fluid pH within that range throughout subsequent use of the viscosified fluid. The term "pH stability" is intended to refer to the resistance of the fluid to change in pH over time. One manner of measuring pH stability involves a determination of  $\phi$ . To determine  $\phi$  of an inventive composition,  $\phi$  of a mixed salt composition is determined and related to the  $\phi$  of one or more of the related single salt systems according to the following equation:

$$\phi = \frac{2 * \phi(A/B)}{\phi(A) + \phi(B)}$$

φ represents a ratio of viscosities and pH changes determined as follows: The fluid is formulated and its initial properties, pH and viscosity at 170 sec<sup>-1</sup>, are measured. Then the fluid is subjected to 16 hours of rolling heat aging at a temperature no greater than T<sub>50</sub>; and the final properties, including pH and viscosity at 170 sec<sup>-1</sup>, are measured. The parameter φ is then determined from the following equation:

$$\varphi = \frac{\text{final viscosity at a given shear rate}}{\text{final pH} - \text{initial pH}}$$

The φ values for the single salt and multiple salt systems are measured similarly and used to measure φ according to the above equation. In one aspect of the invention, inventive two salt systems exhibit a φ of greater than about 1.

This means that the φ<sub>50</sub> of the inventive two salt system is greater than expected based upon the linear relationship between the φ values for the two corresponding single salt systems.

In use, inventive compositions are preferably utilized in exploiting subterranean petroliferous formations as drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer or hole abandonment fluids. For instance, in a preferred use as a hydraulic fracturing fluid, a viscosified mixed salt brine fluid is introduced into a formation at a rate and pressure sufficient to fracture the formation. At first, the fluid leaks off into the rock matrix, building up a filter cake on the rock face. The filter cake then prevents fluid injected thereafter from leaking off significantly. The full force of the applied hydraulic pressure eventually comes to bear upon the rock face, causing the rock to part at the weakest point. As the fracture grows, additional fracturing fluid containing a solid proppant material is introduced. Following this treatment, as much as possible of the introduced fluid is recovered from the formation, but the proppant remains to prevent the complete

closure of the fracture. The propped fracture creates a highly conductive channel extending from the well bore into the formation, making the reservoir more productive.

High viscosity fracturing fluids undergo high shear stress during the introduction of such fluids into a formation. The viscosity of the fluid must be high enough to carry proppant but low enough that excessive friction losses and high well head pumping pressures are not encountered. Polymer degradation is a natural result of shear stresses imposed by pumping, the presence of abrasive materials, and high flow rates through small flow channels. This mechanical degradation accompanies thermal degradation and chemical degradation produced by acid catalyzed hydrolysis of the acetal bonds which are the weakest links along the polymer backbone.

The invention will be further described with reference to the following specific Examples. It will be understood that these Examples are illustrative and not restrictive in nature.

**EXAMPLE ONE**  
**PREPARING INVENTIVE DENSE, VISCOSIFIED**  
**AQUEOUS COMPOSITIONS**

Two salts are selected and prepared by dissolving the salts into water. The following salt combinations are used:

lithium chloride/lithium bromide  
calcium chloride/calcium bromide  
sodium bromide/calcium bromide  
lithium bromide/sodium bromide  
lithium bromide/calcium bromide  
sodium chloride/potassium chloride  
sodium chloride/calcium bromide  
sodium chloride/sodium bromide  
sodium bromide/potassium bromide  
sodium formate/sodium nitrate

- sodium formate/potassium nitrate  
potassium formate/sodium nitrate  
sodium formate/cesium nitrate  
cesium formate/sodium nitrate  
5 potassium formate/cesium nitrate  
cesium formate/potassium nitrate  
lithium formate/cesium nitrate  
cesium formate/lithium nitrate  
potassium formate/calcium nitrate  
10 calcium formate/potassium nitrate  
potassium formate/potassium nitrate  
cesium formate/cesium nitrate  
potassium chloride/potassium bromide  
potassium bromide/calcium bromide  
15 potassium chloride/calcium bromide  
potassium formate/ calcium bromide  
magnesium chloride/calcium chloride  
magnesium chloride/calcium bromide  
magnesium bromide/calcium bromide  
magnesium chloride/magnesium bromide  
20 cesium chloride/cesium bromide  
cesium chloride/sodium chloride  
cesium bromide/sodium chloride  
cesium chloride/sodium bromide  
cesium bromide/sodium bromide  
25 cesium chloride/potassium chloride  
cesium bromide/potassium chloride  
cesium chloride/potassium bromide  
cesium bromide/potassium bromide  
cesium chloride/calcium chloride  
30 cesium bromide/calcium chloride  
cesium chloride/calcium bromide  
cesium bromide/calcium bromide  
cesium bromide/calcium bromide  
calcium chloride/calcium formate  
35 calcium bromide/calcium nitrate  
calcium bromide/cesium bromide  
zinc complex salts/alkali metal or alkaline earth metal salts  
After the salts are dissolved into the water to a density of at least about 9.5, a  
water-soluble or water-dispersible polymer is hydrated into the solution, thus  
viscosifying the solution for advantageous use as a drilling, drill-in, completion,

hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluid. Amounts of each salt in relation to one another are determined such that the resulting viscosified fluid has a  $\tau_{50}$  of at least about 1; a  $\zeta_{50}$  of at least about 1; a  $\omega_{50}$  of at least about 1; a  $\psi_{50}$  of at most about 1; or a  $\phi$  of at least about 1. Preferably, the ratio of the first salt to the second salt in inventive two salt systems is from about 50/1 to about 1/50.

**EXAMPLE TWO**  
**PREPARING INVENTIVE DENSE, VISCOSIFIED  
AQUEOUS COMPOSITION**

10 Inventive dense, viscosified aqueous compositions are prepared according to Example 1 except that the polymer is hydrated into a solution having dissolved therein only one of the salts of a two salt combination. After hydration of the polymer, the second salt in the two salt composition is added either in the form of a dry salt or in a salt solution.

15 EXAMPLE THREE

## **TESTING PROPERTIES OF INVENTIVE DENSE, VISCOSIFIED AQUEOUS COMPOSITIONS**

## Viscosity Measurements

A fluid is prepared as in Example 1 or Example 2 and rheological properties are measured and recorded at 120°F using a rotational viscometer such as the Fann 35 at the following rpms: 600, 300, 200, 100, 6 and 3. Also measured and recorded are the pH of the fluid at 120°F, and the 10 second and 10 minute gels.

## Determining Heat Stability

One "barrel equivalent" (BEQ) of the fluid is hot rolled at a predetermined temperature for 16 hours; and one BEQ of the fluid is hot rolled at the predetermined temperature for 72 hours (or 48/96 hours if time is available for longer testing). A normal 42 gallon barrel has a weight in pounds equal to (42  
5  $\times \rho$ ), where  $\rho$  is the density of the fluid in pounds per gallon. The BEQ is obtained by simply replacing the weight of the barrel in pounds by the weight of the barrel equivalent in grams. This replacement scales the convenient field unit, the barrel, into a workable laboratory size unit, BEQ.

After the rheological properties are recorded from the Fann 35 or equivalent  
10 for the 16/72 hour or 48/96 hour samples, as indicated above, the samples are examined for evidence of sag, break, or settling and the visual observations are logged. The gels of hot rolled samples of inventive compositions are preferably within the range of from about 6 to about 19.

#### Fluid Loss Testing

15 The fluid loss properties of the fluid are determined as follows. A fluid loss test of duration ranging from 30 minutes to 24 hours is performed in the API standard high pressure high temperature (HP-HT) apparatus. If additional time for testing is available, a 48 hour test duration may be preferable. The testing temperature is predetermined, such as, for example, in accordance with the  
20 bottom-hole temperature at which the fluid will be used in the field. The HP-HT apparatus is employed using 250 to 600 psig differential pressure, using, for example, a 50-2000 millidarcy Aloxite disc of diameter of 2.50 inches and thickness of 0.25 inches.

25 The cell in the heating jacket and the fluid in the static oven are preheated until the cell and sample reach the test temperature. While the cell is being heated, the disc is covered with a thin layer of de-ionized water. The cover (lid) for the cell should also be put in place to prevent evaporation.

The fluid being tested is preheated and then poured into the preheated cell. The loaded cell is then prepared for the application of pressure. The cell is pressurized and the temperature adjusted to the target temperature. The discharge valve is then opened, and the filtrate volume is recorded at time intervals such as 1, 5, 7.5, 10, 15, and 30 minutes, and at 1, 2, 4, 16, 24, and/or 48 hours. The fluid loss volume may then be plotted versus  $(\text{time})^{1/2}$ . This plot is, in most cases, substantially linear. If the plot is linear, the fluid loss behavior is considered normal. Whether or not this is the case is noted in the laboratory notebook.

At 24 or 48 hours, the test is stopped and the cell is cooled and depressurized. It is then noted whether any sag, settling or break has occurred in the fluid in the cell during the pressurized phase of testing. The fluid is then decanted and the filter cake thickness is measured.

#### EXAMPLE FOUR

##### $\text{CaCl}_2/\text{CaBr}_2$

The present inventors have discovered that the stability of biopolymers in a calcium-based brine is dramatically improved when the formation of the base brine is optimized with respect to the calcium chloride and calcium bromide content. At equivalent densities, brine fluids containing calcium chloride and calcium bromide exhibit more stable rheological and gel structure properties with biopolymers than do the corresponding pure calcium chloride brines or pure calcium bromide brines. When the pH of the viscosified fluid is buffered with magnesium oxide in the traditional manner, the rheology of calcium chloride/calcium bromide brines is considerably more stable than the equivalent pure calcium chloride system. For brine densities up to 13.0 ppg or more, the stability of calcium chloride/calcium bromide systems is greater than for the corresponding pure calcium bromide systems.

Rheological and gel structure data for 9.0 pounds per gallon (ppg), 10.5 ppg and 13.0 ppg calcium-based brines are reported in Table 2, Table 3 and Table 4, respectively. For each brine, the concentration of calcium chloride and calcium bromide are reported as a percent of the total brine salt present (%TS), which is varied from 100% calcium chloride to 100% calcium bromide for the 9.0 and 10.5 ppg brines and from 45% calcium chloride for the 13 ppg fluid. The enhanced thermal stability, rheology and gel structure properties for the calcium chloride/ calcium bromide brines are clearly depicted when compared with the corresponding pure salt brines--a result which is totally unexpected based on conventional wisdom in the relevant field.

**Table 2**

**9.0 ppg Viscosified Brine  
2 ppg Bio-Polymer & 2 ppb MgO  
Heat Aged 16 & 72 Hours @ 180°F**

CaCl <sub>2</sub> , % TS	100	60	31	0	
CaBr <sub>2</sub> , % TS	0	40	69	100	
Aging Hours	16	72	16	72	16
PV/YP	5/19	5/15	5/15	5/15	5/17
Gels	7/9	4/4	3/3	4/4	10/13
pH	8.8	8.9	8.7	8.8	8.5
Settling	No	No	No	No	No

% TS - Specified salt as a percent of total soluble salt content.

**TABLE 3**

**10.5 ppg Viscosified Brine  
2 ppb Bio-Polymer & 2 ppb MgO  
Heat Aged 16 & 72 Hours @ 180 F**

CaCl <sub>2</sub> , % TS	100	86	60	31	0
CaBr <sub>2</sub> , % TS	0	14	40	69	100
Aging Hours	16 72	16 72	16 72	16 72	16 72
PV/YP	9/7 7/2	9/18 8/12	9/18 8/16	7/21 7/18	7/16 6/12
Gels	0/0 0/0	3/3 1/1	5/7 5/5	6/8 6/7	4/4 2/2
pH	7.4 7.6	7.7 7.8	8.3 8.3	8.6 8.4	8.1 8.5
Settling	Yes Yes	No Yes	No No	No No	No Yes

% TS - Specified salt as a percent of total soluble salt content.

**TABLE 4**

**13.0 ppg Viscosified Brine  
2 ppb Bio-Polymer & 2 ppb MgO  
Heat Aged 16 & 72 Hours @ 180 F**

CaCl <sub>2</sub> , % TS	45	22	16	0
CaBr <sub>2</sub> , % TS	55	78	84	100
Aging Hours	16 72	16 72	16 72	16 72
PV/YP	21/28 24/33	17/21 19/18	16/15 15/15	14/15 -
Gels	9/10 9/10	5/6 3/5	1/1 1/1	1/1 -
pH	6.7 6.8	7.1 7.1	7.5 7.1	7.2 -
Settling	No No	Yes Yes	Yes Yes	Yes -

% TS - Specified salt as a percent of total soluble salt content.

These surprising results were again verified when a Fann Model 50 evaluation was performed on the 10.5 ppg CaCl<sub>2</sub>, 10.5 ppg CaBr<sub>2</sub>, and 10.5 ppg mixed CaCl<sub>2</sub>/CaBr<sub>2</sub> solutions, this type of test being well known in the art.

Results shown in Figure 2 for the two pure halide systems display a continuous rapid decline in brine viscosity with increasing temperature. Unexpectedly, the mixed halide system shows higher viscosity than either pure halide at a given temperature for a broad range from room temperature to well over 220°F. The  
5 brine systems were initially prepared by adding the biopolymer to the brines and then hydrating each system with the same shearing treatment using a Silverson mixer. When the biopolymer is not completely hydrated, its viscosity increases with heating as the biopolymer fully hydrates. In these experiments the Fann 50 supplies the heat. In the single-salt CaCl<sub>2</sub> and single-salt CaBr<sub>2</sub>  
10 experiments the viscosity did not increase when the fluids were heated, indicating that the biopolymer had been fully hydrated. However, with the mixed salt CaCl<sub>2</sub>/CaBr<sub>2</sub> system, the viscosity did increase early in the experiment. In order to establish whether this observation was the result of biopolymer hydration, the experiment was repeated; but this time the  
15 CaCl<sub>2</sub>/CaBr<sub>2</sub> mixture was blended from samples of viscosified CaCl<sub>2</sub> which had already been proven to be fully hydrated and of viscosified CaBr<sub>2</sub> which had already been proven to be fully hydrated. This new mixture was undeniably fully hydrated, and yet the results of the repeat experiment were almost exactly as before. This shows that the increase in viscosity seen with the two-salt mixture is not a hydration effect but a true indication of increased stability in  
20 the two-salt mixture in comparison with the corresponding single-salt systems of equal density.

As was mentioned above, T<sub>50</sub> is defined as the temperature at which a fluid's viscosity reaches 50% of its original value measured at about room temperature. The surprising relationship between T<sub>50</sub> and percent CaBr<sub>2</sub> in the  
25 10.5 ppg system is clearly demonstrated in Figure 3.

Application of this invention to optimization of calcium-based brines can result in viscosified brines having unexpected and greatly improved stability.

This substantial increase in stability permits the practical use of these brines for things such as drilling brines, drill-in fluids, fluid loss control pills and hydraulic fracturing fluids.

#### EXAMPLE FIVE

##### NaBr/CaBr<sub>2</sub>

5        The present inventors have discovered that by taking a CaBr<sub>2</sub> solution which can be viscosified with xanthan gum and weighting the solution to a higher density with dry NaBr, instead of CaBr<sub>2</sub> or CaCl<sub>2</sub>, the time required to reach maximum viscosity is reduced substantially. Results of adding 3 pounds per barrel (ppb) of xanthan gum to 14.2 ppg solutions, one a pure CaBr<sub>2</sub> solution and the other a mixed CaBr<sub>2</sub>/NaBr solution, are shown in Table 5.

10      Surprisingly, the two salt mixture began to viscosify after only 10 minutes of shearing, while the CaBr<sub>2</sub> solution required significantly more time and shear. The yield point (YP) for a solution is a good measure for the degree of polymer activation. The YP for the mixed CaBr<sub>2</sub>/NaBr salt system reached 12% of its final value in the first 10 minutes while the pure CaBr<sub>2</sub> system had none of its ultimate value. The two salt mixture fully viscosified within 22 hours of stirring after shearing while the CaBr<sub>2</sub> solution did not do so even after 42 hours of stirring.

Table 5 14.2 ppg Solutions + 3 ppb of Xanthan Gum								
	CaBr <sub>2</sub>	CaBr <sub>2</sub> /NaBr	CaBr <sub>2</sub>	CaBr <sub>2</sub> /NaBr	CaBr <sub>2</sub>	CaBr <sub>2</sub> /NaBr	CaBr <sub>2</sub>	CaBr <sub>2</sub> /NaBr
600	22	44	30	71	83	144	104	148
300	11	26	16	47	56	106	72	108
6	0	2	0	6	7	24	13	25
3	0	1	0	4	5	19	9	20
Gels	0/0	1/1	0/0	4/5	5/8	20/48	10/21	24/56
PV	11	18	14	24	27	38	32	40
YP	0	8	2	23	29	68	40	68
Method	Sheared- Time RPM	10 Min. 4000	Sheared- Time RPM	18 min. 4000	Stirred - Time	22 hours	Stirred - Time	42 hours

Figure 4 shows the  $T_m$  for 12.5 ppg NaBr, mixtures of 13.0 ppg CaBr<sub>2</sub>/NaBr, and viscosity data for pure CaBr<sub>2</sub>. The 13.0 ppg pure CaBr<sub>2</sub> solution shows no  $T_m$ , but with the introduction of NaBr, the  $T_m$  increases with increasing concentrations of NaBr.

- 5 In Figure 5,  $T_{50}$  is plotted versus the pounds of NaBr per barrel (ppb) of fluid. Unexpectedly, NaBr was found to substantially increase the  $T_{50}$  of the mixed CaBr<sub>2</sub>/NaBr brine fluids. This shows that the mixed salt system provides higher thermal stability than the pure CaBr<sub>2</sub> solution.

To determine whether the mixed CaBr<sub>2</sub>/NaBr salt system also increases  
10 the thermal stability of other polysaccharides, such as pre-gelatinized starch,  
which show no transition temperature, a heating and cooling cycle was  
conducted on 12 ppb of a pre-gelatinized starch added to a 13.0 ppg pure CaBr<sub>2</sub>  
solution and compared with 12 ppb of pre-gelatinized starch added to a 13.0  
ppg mixed CaBr<sub>2</sub>/NaBr salt system. The mixed salt system was prepared by  
15 taking 11.0 ppg CaBr<sub>2</sub> and weighting it up with dry NaBr until a 13.0 ppg  
solution was obtained. Each solution was heated at 2.56 °F/minute in 20°F  
increments at a shear rate of 170 sec<sup>-1</sup> beginning at 120°F and then quick-  
cooled to 70°F. By using this heating and cooling cycle, the breakdown of the

pre-gelatinized starch was determined and is shown in Figure 6. The percent viscosities of both solutions begin to decrease to about 150°F and then stop decreasing. However, when heated to 240°F and cooled to 70°F, the pre-gelatinized starch in the 13.0 ppg pure CaBr<sub>2</sub> solution showed dramatic 5 decrease in the retained percent viscosity while in the mixed salt system this phenomena occurred only after the higher temperature of 260°F. As such, Figure 6 shows that the mixed salt system increases the thermal stability of the pre-gelatinized starch compared with the pure CaBr<sub>2</sub> solution.

#### EXAMPLE SIX

10

##### LiBr/NaBr

Table 6 presents T<sub>50</sub> data for the LiBr/NaBr mixed salt system. Two different ratios of LiBr to NaBr were tested and in both cases the data show improved stability for the xanthan-viscosified LiBr/NaBr mixed salt system in comparison with viscosified pure LiBr and viscosified pure NaBr. For 15 example, if one interpolates linearly between the T<sub>50</sub> for 12.5 ppg LiBr, 114°F, and the T<sub>50</sub> for 12.5 ppg NaBr, 291°F to predict the T<sub>50</sub> of the mixture, the actually observed T<sub>50</sub> values for the LiBr/NaBr mixtures are greater than those predicted. This comparison is illustrated graphically in Figure 7 in which the T<sub>50</sub> values are plotted versus the pounds of LiBr added per barrel of fluid. The 20 slightly upward curvature of the line joining pure NaBr (at 0) and pure LiBr shows the extra stabilization of the system when the brines are mixed.

**TABLE 6**

<b>T<sub>50</sub> Data on</b>			
<b>Mixed Salts</b>			
<b>Mixed Salt</b>	<b>T<sub>50</sub> (A/B)</b>	<b>T<sub>50</sub> (A)</b>	<b>T<sub>50</sub> (B)</b>
	<b>(°F)</b>	<b>(°F)</b>	<b>(°F)</b>
5 <b>System A/B</b>			
LiBr/NaBr (50/50)	220	114	291
LiBr/NaBr (25/75)	263	114	291

**EXAMPLE SEVEN****LiBr/CaBr<sub>2</sub>**

10      Table 7 presents T<sub>50</sub> data for the LiBr/CaBr<sub>2</sub> mixed salt system. When LiBr was added to CaBr<sub>2</sub>, extreme improvement was observed in the stability for the xanthan-viscosified LiBr/CaBr<sub>2</sub> mixed salt system in comparison with viscosified pure LiBr and viscosified pure CaBr<sub>2</sub>. For example, as one can see clearly in Figure 8, observed data is significantly greater than that predicted by  
15      linear interpolation.

**TABLE 7**

<b>T<sub>50</sub> Data on</b>			
<b>Mixed Salts</b>			
<b>Mixed Salt</b>	<b>T<sub>50</sub> (A/B)</b>	<b>T<sub>50</sub> (A)</b>	<b>T<sub>50</sub> (B)</b>
	<b>(°F)</b>	<b>(°F)</b>	<b>(°F)</b>
20 <b>System A/B</b>			
LiBr/CaCl <sub>2</sub>	266	114	184.8

**EXAMPLE EIGHT****NaCl/KCl**

Table 8 presents  $T_{50}$  data for the 9.0 ppg NaCl/KCl mixed salt system. The data showed no improvement in heat stability for the xanthan-viscosified 5 NaCl/KCl mixed salt system in comparison with viscosified pure NaCl and viscosified pure KCl. The data obtained for this two-salt system show no improvement over the corresponding single salt systems. Accordingly, in those systems wherein there is an observable improvement with the mixed salt systems over the corresponding single salts, said improvement is unexpected. 10 Additionally, various systems which show no improvement in heat stability do show, for example, good shear stability and/or fluid loss control characteristics.

**TABLE 8**

<b>T<sub>50</sub> Data on Mixed Salts</b>			
	<b>Mixed Salt</b>	T <sub>50</sub> (A/B)	T <sub>50</sub> (A)
	<b>System A/B</b>	(°F)	(°F)
5	NaCl/KCl	300	300

**EXAMPLE NINE****NaCl/NaBr**

As with the CaCl<sub>2</sub>/CaBr<sub>2</sub> system discussed above, the rheological and fluid loss data presented in Table 9 demonstrate the increased effectiveness and stability with time of the mixed halide salt system when compared to the single NaCl salt system. This unexpected stability occurs in an especially important temperature range and greatly extends the useful range for these drilling brine systems.

**Table 9**  
**9.5 ppg Sodium-based Drilling Brines**

System	NaCl	NaCl/NaBr	NaCl	NaCl/NaBr	NaCl	NaCl/NaBr
Rheological Properties	Test Temp	Room	Time Temp	16 Hours 260 °F	Time Temp	72 Hours 260 °F
6/3 RPM	25/23	23/22	23/21	22/20	9/7	17/15
Gels	24/27	22/25	23/20	20/24	7/8	15/16
PV	17	19	9	9	10	11
YP	49	47	45	43	24	37
Sample Temp, °F	76	77	120	120	120	120
HTHP Fluid Loss Test						
Temperature, °F			260	260		
Delta Pressure, psi			500	500		
Core, md			500	500		
30 Minutes, ml			15	4		
48 Hours, ml			85	73		

Table 10 presents  $T_m$  and  $T_{50}$  data for the 9.0 ppg NaCl/NaBr mixed salt system. The data for pure NaBr are estimated. The analysis suggests no improvement in stability for the xanthan-viscosified NaCl/NaBr mixed salt system in comparison with the corresponding viscosified pure single salts, in contrast with the Table 9 data just discussed above.

TABLE 10

<b>Mixed Salts</b>						
<b>Mixed Salt</b>	$T_m$ (A/B)	$T_m$ (A)	$T_m$ (B)	$T_{50}$ (A/B)	$T_{50}$ (A)	$T_{50}$ (B)
<b>System A/B</b>	(°F)	(°F)	(°F)	(°F)	(°F)	(°F)
NaCl/NaBr	272	272	≈270	300	300	≈290

What is the resolution to this apparent contrast? First, the Table 9 data showed little or no difference at 16 hours, and only at 72 hours did a significant difference appear; the data in Table 10 are from tests which span less than two hours. If differences only appear after an extended duration they cannot be seen in data such as those of Table 10. Second, the Table 10  $T_m$  and  $T_{50}$  data are all relatively high temperatures and the densities of the brines involved are all relatively low, 9.0 ppg. For other mixed brine systems, we have such data for generally higher brine densities, and often observe  $T_m$  and  $T_{50}$  values for the viscosified pure salts which are much lower than those of Table 10. In mixed salt brines having higher densities and lower  $T_m$  and  $T_{50}$  values for the viscosified pure salts, it is apparently easier to observe the benefit of improved stability due to the presence of the mixed brines when observing over the course of short experiments such as those of Table 10. The same phenomenon likely explains the Table 8  $T_{50}$  data for the 9.0 ppg NaCl/KCl mixed salt system

**EXAMPLE TEN****NaBr/KBr**

Table 11 presents  $T_{50}$  data for the 11.4 ppg NaBr/KBr mixed salt system. The data for pure NaBr are estimated. The analysis shows improvement in stability for the xanthan-viscosified NaBr/KBr mixed salt system in comparison with the corresponding viscosified pure single salts.

**Table 11**

<b><math>T_{50}</math> Data on Mixed Salts</b>			
	<b>Mixed Salt</b>	$T_{50(A/B)}$	$T_{50(A)}$
	<b>System A/B</b>	(°F)	(°F)
10	NaBr/KBr (50/50)	300	<291
5			300

**EXAMPLE ELEVEN****NaHCO<sub>2</sub>/NaNO<sub>3</sub>**

Table 12 presents  $T_m$  data for the 11.0 ppg NaHCO<sub>2</sub>/NaNO<sub>3</sub> mixed salt system. The data showed substantial improvement in stability for the xanthan-viscosified NaHCO<sub>2</sub>/NaNO<sub>3</sub> mixed salt system in comparison with viscosified pure NaHCO<sub>2</sub> and viscosified pure NaNO<sub>3</sub>. The 11.0 ppg mixture of NaHCO<sub>2</sub>/NaNO<sub>3</sub>, was a 50/50 mixture by weight of 11.0 ppg NaHCO<sub>2</sub> which has a  $T_m$  of 356°F and 11.0 ppg NaNO<sub>3</sub>, which has a  $T_m$  of 290°F. Interpolation between these data predicts a  $T_m$  of 323°F, whereas a substantially higher value, 330°F, was observed. This comparison is illustrated graphically in Figure 9 in which the  $T_{50}$  values are plotted versus the pounds of NaNO<sub>3</sub> added per barrel of fluid. The slightly upward curvature of the line joining pure NaHCO<sub>2</sub> (at 0)

and pure NaNO<sub>3</sub> shows the extra stabilization of the system when the brines are mixed.

**Table 12**

<b>T<sub>M</sub> Data on Mixed Salts</b>			
<b>Mixed Salt</b>	<b>T<sub>M</sub>(A/B)</b>	<b>T<sub>M</sub>(A)</b>	<b>T<sub>M</sub>(B)</b>
<b>System A/B</b>	(°F)	(°F)	(°F)
NaHCO <sub>2</sub> /NaNO <sub>3</sub>	330	356	290

### **EXAMPLE TWELVE**

#### **KBr/CaBr<sub>2</sub>, KHCO<sub>2</sub>/CaBr<sub>2</sub>, and KBr/Ca(HCO<sub>2</sub>)<sub>2</sub>**

Table 13 presents T<sub>50</sub> data for five mixed salt systems: a 13.0 ppg LiBr/CaBr<sub>2</sub> mixed salt system, a 13.0 ppg NaBr/CaBr<sub>2</sub> mixed salt systems, a 13.0 ppg KBr/CaBr<sub>2</sub> mixed salt system, a 13.2 ppg KHCO<sub>2</sub>/CaBr<sub>2</sub> mixed salt system, and a 13.2 ppg KBr/Ca(HCO<sub>2</sub>)<sub>2</sub> mixed salt system. The LiBr/CaBr<sub>2</sub> and the NaBr/CaBr<sub>2</sub> mixed salt systems have been discussed above. We were able to produce a solution comprising 42.3 weight % CaBr<sub>2</sub> and 4.7 weight % KHCO<sub>2</sub> and having a density of 13.2 ppg. Adding just a little more KHCO<sub>2</sub> would have led to formation of a precipitate; even so, it was found that the T<sub>50</sub> of the xanthan-viscosified KHCO<sub>2</sub>/CaBr<sub>2</sub> mixed brine is substantially greater than the T<sub>50</sub> of a comparable xanthan-viscosified CaBr<sub>2</sub> brine.

The table also shows that the  $T_{50}$  of the xanthan-viscosified KBr/CaBr<sub>2</sub> mixed brine is substantially greater than the  $T_{50}$  of a comparable xanthan-viscosified CaBr<sub>2</sub> brine.

Table 13

5

 $T_{50}$  Data on

## Mixed Salts

	Density	Mixed Salt System A/B	$T_{50}$ (A/B)	$T_{50}$ (A)	$T_{50}$ (B)
			(°F)	(°F)	(°F)
10	13.0 ppg	LiBr/CaBr <sub>2</sub>	266	114	185
	13.0 ppg	NaBr/CaBr <sub>2</sub> (11.0 ppg + NaBr)	273	-	185
	13.0 ppg	KBr/CaBr <sub>2</sub>	261		185
	13.2 ppg	KHCO <sub>2</sub> /CaBr <sub>2</sub>	231		185
	13.2 ppg	KBr/Ca(HCO <sub>2</sub> ) <sub>2</sub>	231		

## EXAMPLE THIRTEEN

15

MgCl<sub>2</sub>/CaCl<sub>2</sub>

Calcium chloride at 10.5 ppg was converted into a drilling brine by the addition of viscosifying polymers and conventional brine-based buffer at 2 pounds per barrel. Similar MgCl<sub>2</sub>/CaCl<sub>2</sub> systems were prepared wherein some of the calcium chloride was replaced with an equivalent amount of magnesium chloride. The resulting drilling brines were then hot rolled at 180°F for 16 and 20 72 hours, and their drilling properties were measured. The resulting data are shown in Table 14. The trends observed for the YP and Gel structure indicate

the increased stability obtained with the mixed salt brine system compared to the pure  $\text{CaCl}_2$  system. This unexpected increase in stability is amply demonstrated with the plot of YP versus pounds  $\text{MgCl}_2$  in the drilling brine, shown in Figure 10.

5

**TABLE 14**
**10.5 ppg  $\text{CaCl}_2/\text{MgCl}_2$  Drilling Brines  
Rheological and Gel Properties**

Pounds $\text{MgCl}_2$ per Barrel	0	4.0	14.1	18.7	28.1
<b>16 Hours @ 180°F</b>					
6/3 RPM	1/1	6/4	7/5	6/5	8/6
Gels	0/0	5/5	5/6	5/5	7/8
PV	9	10	9	9	9
YP	7	19	20	19	21
Sample Temperature, °F	121	120	120	120	120
<b>72 Hours @ 180°F</b>					
6/3 RPM					
Gels	0/0	1/0	2/1	3/2	3/2
PV	0/0	0/0	2/2	2/3	3/3
YP	7	9	9	9	10
Sample Temperature, °F	122	120	120	120	120

**EXAMPLE FOURTEEN**
 **$\text{MgCl}_2/\text{CaBr}_2$  and  $\text{MgBr}_2/\text{CaCl}_2$** 

Brine based drilling fluids at 11.0 ppg were prepared from pure magnesium chloride and pure calcium bromide. Each fluid included the same amount of biopolymer and conventional brine buffer (2 ppg), and was prepared in an identical manner. Mixed brine fluids were prepared by mixing the

appropriate quantities of each formulated pure salt system. The drilling brine fluids presented in Tables 15-17 were prepared as described, subjected to the aging and heat aging conditions specified, and then the rheological and gel properties were measured and recorded. Quite unexpectedly the 35%  
5 MgCl<sub>2</sub>/65% CaBr<sub>2</sub> heat aged sample exhibited substantially increased values for properties across the board compared to either pure salt system. This fluid exhibited both increased gel and low end rheological properties, and the properties of this system could easily be optimized even with reduced polymer content. Even the 65% MgCl<sub>2</sub>/35% CaBr<sub>2</sub> heat aged sample yielded improved  
10 properties compared to the pure CaBr<sub>2</sub> system.

**Table 15**

**11.0 ppg MgCl<sub>2</sub>/CaBr<sub>2</sub>-based Drilling Brines  
Initial Rheological Properties**

System	100% MgCl <sub>2</sub>	65/35% MgCl <sub>2</sub> /CaBr <sub>2</sub>	35/65% MgCl <sub>2</sub> /CaBr <sub>2</sub>	100% CaBr <sub>2</sub>
Rheological Properties	Room Temp	Room Temp	Room Temp	Room Temp
6/3 RPM	20/18	15/14	12/11	6/8
Gels	21/24	14/19	11/16	12/13
PV	31	25	16	11
YP	38	35	29	22
Sample Temp, °F	120	120	120	120

**Table 16**

**11.0 ppg MgCl<sub>2</sub>/CaBr<sub>2</sub>-based Drilling Brines  
Heat-aged Rheological Properties**

System	100% MgCl <sub>2</sub>	65/35% MgCl <sub>2</sub> /CaBr <sub>2</sub>	35/65% MgCl <sub>2</sub> /CaBr <sub>2</sub>	100% CaBr <sub>2</sub>
Rheological Properties	16 Hours 180°F	16 Hours 180°F	16 Hours 180°F	16 Hours 180°F
6/3 RPM	17/14	15/12	39/36	6/4
Gels	18/21	14/17	39/44	5/6
PV	22	23	61	12
YP	32	37	43	20
Sample Temp, °F	120	120	120	120

**Table 17**

**11.0 ppg MgCl<sub>2</sub>/CaBr<sub>2</sub>-based Drilling Brines  
Heat-aged Rheological Properties**

System	100%	65/35%	35/65%	100%
	MgCl <sub>2</sub>	MgCl <sub>2</sub> /CaBr <sub>2</sub>	MgCl <sub>2</sub> /CaBr <sub>2</sub>	CaBr <sub>2</sub>
Rheological Properties	62 Hours 180°F	62 Hours 180°F	62 Hours 180°F	62 Hours 180°F
6/3 RPM	19/16	19/16	33/29	6/4
Gels	18/20	16/19	27/29	6/6
PV	20	28	60	11
YP	36	42	30	21
Sample Temp, °F	120	120	120	120

**EXAMPLE FIFTEEN**

**CaBr<sub>2</sub>/Ca(NO<sub>3</sub>)<sub>2</sub>**

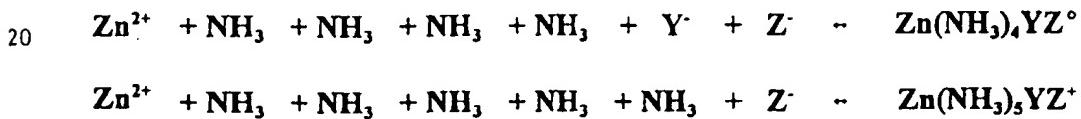
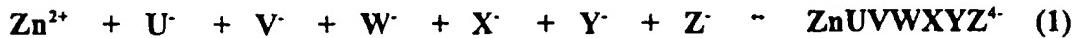
Table 18 presents T<sub>m</sub> data for the 13.0 ppg CaBr<sub>2</sub>/Ca(NO<sub>3</sub>)<sub>2</sub> mixed salt system. The T<sub>m</sub> for the viscosified CaBr<sub>2</sub>/Ca(NO<sub>3</sub>)<sub>2</sub> mixture is surprisingly higher than that of viscosified pure Ca(NO<sub>3</sub>)<sub>2</sub>. The stabilization observed in the mixed salt system is also apparent from the fact that the mixture has a T<sub>m</sub> value whereas viscosified pure CaBr<sub>2</sub> does not even show a transition from which to measure a T<sub>m</sub>.

**Table 18**

<b>T<sub>m</sub> Data on</b>			
<b>Mixed Salts</b>			
<b>Mixed Salt</b>	<b>T<sub>m</sub> (A/B)</b>	<b>T<sub>m</sub> (A)</b>	<b>T<sub>m</sub> (B)</b>
	<b>System A/B</b>	(°F)	(°F)
CaBr <sub>2</sub> /Ca(NO <sub>3</sub> ) <sub>2</sub> (50/50)	225	N/A	222

**EXAMPLE SIXTEEN****Zinc Complex Salts Mixed with Alkali Metal and Alkaline Earth Metal Salts**

10 Table 19 presents data for three mixed salt systems: a 17.5 ppg CaZnBr<sub>4</sub>/Ca<sub>3</sub>(ZnBr<sub>5</sub>)<sub>2</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/NaBr mixed salt system (or more conventionally represented as a CaBr<sub>2</sub>/ZnBr<sub>2</sub>/NaBr mixed salt system), and two different 17.5 ppg CaZnBr<sub>4</sub>/Ca<sub>3</sub>(ZnBr<sub>5</sub>)<sub>2</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub> mixed salt systems (or more conventionally represented as a CaBr<sub>2</sub>/ZnBr<sub>2</sub> mixed salt system).  
15 These solutions were formulated initially from 19.2 ppg CaBr<sub>2</sub>/ZnBr<sub>2</sub> mixed salt clear brine and 13.2 ppg CaBr<sub>2</sub>; then additional solid salt containing bromide anion was added to the formulation to assure that the zinc would be complexed to a significant extent according to the following chemical reaction:



where U<sup>-</sup>, V<sup>-</sup>, W<sup>-</sup>, X<sup>-</sup>, Y<sup>-</sup>, and Z<sup>-</sup> are zinc complexing agents such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SCN<sup>-</sup>, CNO<sup>-</sup>, citrate anion, etc.

Robert M. Smith, Critical Stability Constants, Volume 4, p. 115, Volume 5, p. 421, and Volume 6, page 459, (New York: Plenum Press, 1989). The above list can obviously be augmented with non-ionic zinc complexing agents such as NH<sub>3</sub>, H<sub>2</sub>S, CH<sub>3</sub>I, and various other organics, such as, for example, primary amines like isopropanolamine, secondary amines such as methyl ethanolamine, and tertiary amines, including triethanolamine. Additionally, two or more of the complexing agents, Y<sup>-</sup> and Z<sup>-</sup>, may be supplied by different parts of a single moiety. For example, both the citrate and oxalate anion molecules comprise more than one carboxylate group, two of which can be attached as ligands to a given zinc ion just as easily as can each carboxylate group serve as a ligand for separate zinc ions.

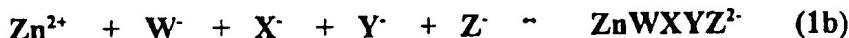
10

Possible variants of Reaction 1 include the following:



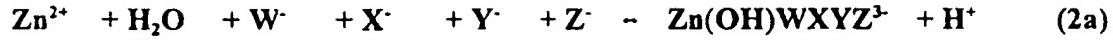
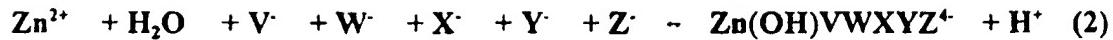
and

15

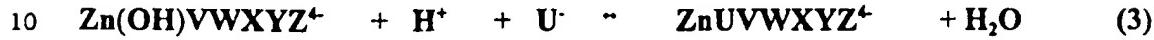


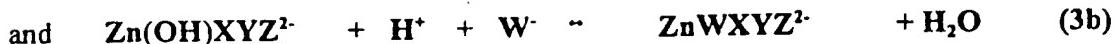
20

In the Table 19 systems, U<sup>-</sup>, V<sup>-</sup>, W<sup>-</sup>, X<sup>-</sup>, Y<sup>-</sup>, and Z<sup>-</sup> are all embodied in Reaction 1 as the bromide anion and therefore ZnUVWXYZ<sup>4-</sup> as the ZnBr<sub>6</sub><sup>4-</sup> anion, ZnVWXYZ<sup>3-</sup> as the ZnBr<sub>5</sub><sup>3-</sup> anion, ZnWXYZ<sup>2-</sup> as the ZnBr<sub>4</sub><sup>2-</sup> anion, etc. The reason for the need to get the bromide anion concentration high is seen in another variant of Reaction 1, given below as Reaction 2, and its further variants:



Since the Table 19 systems are water-based, there is therefore a tendency for  
 5 the zinc to hydrolyze in accordance with Reaction 2, releasing H<sup>+</sup> and reducing  
 the pH. At low pH, the thermal decomposition of biopolymers and common  
 fluid loss control materials is accelerated. To avoid this undesirable  
 consequence, consider the combination of Reactions 1 and 2, which is Reaction  
 3 and its variants, below:





In water-based zinc brines, accordingly, having an excess of bromide anion or any other strongly zinc-complexing agent will, through the action of LeChatelier's principle upon Reaction 3, shift the equilibrium to the right and diminish the concentration of  $\text{H}^+$ . Notice in Table 19 that the highest pH values are seen in the last column, where the highest level of added salt and lowest rate of thermal decomposition of biopolymers and common fluid loss control materials are also to be found. Another undesirable consequence to avoid can be seen in further variants of Reaction 2, below:



Reactions 2c through 2e, and the like, are undesirable because they would further reduce the pH. However, having an excess of bromide anion or any other strongly zinc-complexing agent to serve in the roles of V<sup>-</sup>, W<sup>-</sup>, and X<sup>-</sup>, in

these reactions will, through the action, again, of LeChatelier's principle shift the equilibria to the left and diminish the concentration of H<sup>+</sup>.

Considering the center two columns in Table 19, it is apparent that adding about 20 ppb of calcium bromide is somewhat more effective in 5 increasing the pH and extending the durability of the formulation than adding about the same weight of NaBr.

It should be noted that while the added soluble salts were acting in the role of a pH buffer, conventional pH buffering agent was added to each drill-in fluid given in Table 19. The amount added would have been, for most other 10 base brine systems, sufficient to keep the pH well above 5. Instead, none of the fluids in Table 19 had such a relatively high pH. This fact is a reflection of the strong pH control resulting from the base brine chemistry (Reactions 1-3 and variants) and negligible pH control induced by the presence of the 10 ppb of pH buffering agent. The point is underscored that obtaining a desirably low rate of 15 thermal decomposition is possible especially by proper control of the pH through control of brine chemistry (especially Reactions 3 and variants), rather than through the addition of conventional pH buffering agents.

- 53 -

**TABLE 19**  
**17.5 ppg Viscosified ZnBr<sub>2</sub>-based Brine**  
**2 ppb Bio-Polymer, 4 ppb Fluid Loss Control Material, & 10 ppb pH Buffer**  
**Heat Aged 16, 40, & 96 Hours @ 180°F**

	NaBr added, ppb	20.25	0	0	0	0
CaBr <sub>2</sub> added, ppb	0		19.5			83.9
Base Brine System	17.5 ppg CaZnBr <sub>4</sub> /Ca <sub>3</sub> (ZnBr <sub>5</sub> ) <sub>2</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /NaBr	17.5 ppg CaZnBr <sub>4</sub> /Ca <sub>3</sub> (ZnBr <sub>5</sub> ) <sub>2</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub>		17.5 ppg CaZnBr <sub>4</sub> /Ca <sub>3</sub> (ZnBr <sub>5</sub> ) <sub>2</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub>		
Heat Aging Hours	16	40	96	16	40	96
PV/YP	53/75	49/34	- / - <sup>a</sup>	60/82	60/78	34/ 9 <sup>b</sup>
Gels	23/17	7/ 5	- / - <sup>a</sup>	23/17	7/ 5	1/ 1 <sup>b</sup>
pH	2.76	2.57	- <sup>a</sup>	3.10	2.82	2.74 <sup>b</sup>
Settling	No	No	Yes	No	Yes	No
Reference	BW3-62		BW3-58		RH2-6	

Note a: The pH and rheology were not measured because the biopolymer and fluid loss control material had very severely degraded at this point in the rolling heat-aging.

Note b: The biopolymer and fluid loss control material had degraded but not so severely as in the case described in Note a.

Note c: The biopolymer and fluid loss control material had degraded but not so severely as in the case described in Note b.

Table 20 presents data for the following eleven mixed salt clear brine systems:

- A 15 ppg ZnBr<sub>2</sub>/CaBr<sub>2</sub> mixed salt system;  
 A 15 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub> mixed salt system;  
 A 15 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/NaBr mixed salt system;  
 A 15 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/CaCl<sub>2</sub> mixed salt system;  
 A 15 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/NaCl mixed salt system;  
 A 17 ppg ZnBr<sub>2</sub>/CaBr<sub>2</sub> mixed salt system;  
 A 17 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub> mixed salt system;  
 A 17 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/NaBr mixed salt system;  
 A 17 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/CaCl<sub>2</sub> mixed salt system;  
 A 17 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/NaCl mixed salt system; and  
 A 17 ppg CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>/CaBr<sub>2</sub>/CaCl<sub>2</sub> mixed salt system.

---

**Table 20**

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**15.0 ppg and 17.0 ppg ZnBr<sub>2</sub>/CaBr<sub>2</sub>- and CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>-based Clear Brines**  
**The Effect of Added Soluble Salt on pH**

System	Base Brine Density (ppg)	Weight-up Chemical	Weight Added (ppb)	pH
ZnBr <sub>2</sub> /CaBr <sub>2</sub>	15.0	None	0.0	3.07
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub>	15.0	CaBr <sub>2</sub>	329.9	5.37
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /NaBr	15.0	NaBr	206.6	4.88
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /CaCl <sub>2</sub>	15.0	CaCl <sub>2</sub>	167.0	4.88
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /NaCl	15.0	NaCl	109.3	4.30
ZnBr <sub>2</sub> /CaBr <sub>2</sub>	17.0	None	0.0	2.09
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub>	17.0	CaBr <sub>2</sub>	206.1	4.19
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /NaBr	17.0	NaBr	146.8	3.39
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /CaCl <sub>2</sub>	17.0	CaCl <sub>2</sub>	123.4	3.97
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /NaCl	17.0	NaCl	90.8	3.19
CaZnBr <sub>4</sub> /Ca <sub>2</sub> ZnBr <sub>6</sub> /CaBr <sub>2</sub> /CaCl <sub>2</sub>	18.2	CaCl <sub>2</sub>	330.0	3.71

Comparisons of the various salt additives are best made on a molar basis, as is seen below. In Table 21, we have expanded the Table 20 data from 11 systems to 48, by adding data from 37 systems very closely related to the 11 from Table 20. Additionally, molar-basis data are given.

Table 21

15.0 ppg and 17.0 ppg ZnBr<sub>2</sub>/CaBr<sub>2</sub>- and CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>-based Clear

**Brines**  
**The Effect of Added Soluble Salt on pH**

Moles Zinc	Moles Ca <sub>2+</sub>	Moles Na <sup>+</sup>	Moles Cl <sup>-</sup>	Moles Br <sup>-</sup>	Moles I <sup>-</sup>	Molar Ratio [Total X: Zn]	pH
1.12	2.30	0	0	3.42	0	3.04	3.07
0.68	1.40	1.43	0	3.51	0	5.12	4.42
0.68	1.40	1.91	0	3.99	0	5.83	4.85
0.68	1.40	2.01	0	4.09	0	5.98	4.88
0.29	3.20	0	0	3.49	0	11.90	5.07
0.29	3.70	0	0	3.99	0	13.61	5.27
0.29	3.80	0	0	4.09	0	13.95	5.33
0.29	3.85	0	0	4.14	0	14.12	5.35
0.29	3.90	0	0	4.19	0	14.29	5.37
0.82	3.51	0	1.84	2.50	0	5.28	4.47
0.82	4.41	0	2.74	2.50	0	6.38	4.80
0.82	4.59	0	2.92	2.50	0	6.60	4.82
0.82	4.68	0	3.01	2.50	0	6.71	4.88
1.00	2.03	0.84	0.84	3.03	0	3.89	3.53
1.00	2.03	1.70	1.70	3.03	0	4.74	4.29
1.00	2.03	1.87	1.87	3.03	0	4.92	4.30
1.46	2.99	0	0	4.45	0	3.04	2.09
1.23	2.51	0.75	0	4.49	0	3.65	2.81
1.23	2.51	1.23	0	4.88	0	4.04	3.30
1.23	2.51	1.33	0	5.08	0	4.12	3.34
1.23	2.51	1.38	0	5.12	0	4.16	3.39
1.23	2.51	1.43	0	5.17	0	4.20	3.39
1.03	3.46	0	0	4.49	0	4.37	3.28
1.03	3.98	0	0	4.99	0	4.85	3.90
1.03	4.06	0	0	5.09	0	4.95	4.05
1.03	4.11	0	0	5.14	0	5.00	4.09
1.03	4.16	0	0	5.19	0	5.05	4.19
1.30	3.62	0	0.96	3.96	0	3.78	2.48
1.30	4.52	0	1.86	3.96	0	4.47	3.56
1.30	4.70	0	2.04	3.96	0	4.61	3.84
1.30	4.79	0	2.13	3.96	0	4.88	3.97
1.40	2.85	0.44	0.44	4.24	0	3.36	2.37
1.40	2.85	1.30	1.30	4.24	0	3.97	3.01

Table 21 (continued)

15.0 ppg and 17.0 ppg ZnBr<sub>2</sub>/CaBr<sub>2</sub>- and CaZnBr<sub>4</sub>/Ca<sub>2</sub>ZnBr<sub>6</sub>-based Clear

**Brines**

**The Effect of Added Soluble Salt on pH**

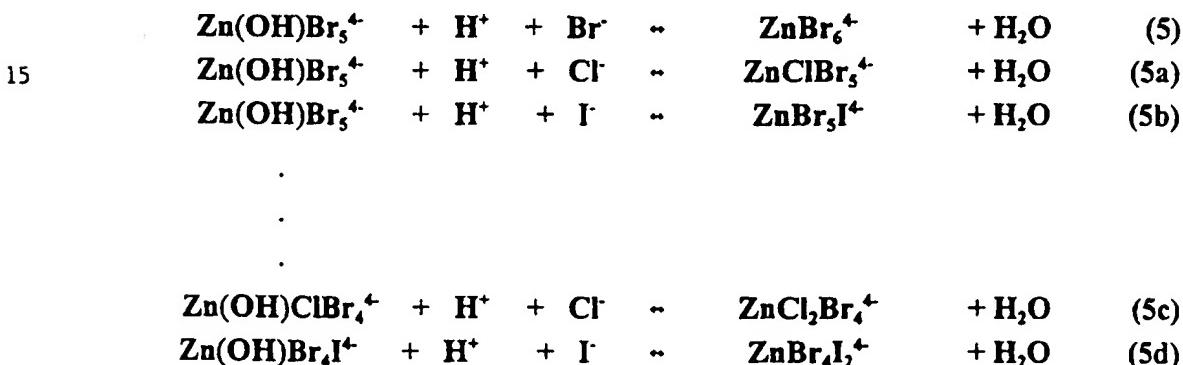
	Moles Zinc	Moles Ca <sub>2+</sub>	Moles Na <sup>+</sup>	Moles Cl <sup>-</sup>	Moles Br <sup>-</sup>	Moles I <sup>-</sup>	Molar Ratio [Total X: Zn]	pH
5	1.40	2.85	1.47	1.47	4.24	0	4.09	3.17
	1.40	2.85	1.55	1.55	4.24	0	4.15	3.19
	1.46	2.99	0	0	4.45	0	3.04	2.09
	1.46	3.04	0	0	4.45	0.06	3.08	2.23
	1.46	3.10	0	0	4.45	0.11	3.12	2.31
	1.46	3.27	0	0	4.45	0.29	3.24	2.35
10	1.46	3.45	0	0	4.45	0.46	3.36	2.53
	1.46	3.62	0	0	4.45	0.63	3.47	2.62
	1.46	3.82	0	0	4.45	0.83	3.61	2.81
	1.46	4.14	0	0	4.45	1.15	3.83	3.16
	1.46	4.42	0	0	4.45	1.44	4.02	3.35
	1.46	4.54	0	0	4.45	1.55	4.10	3.46
15	1.46	4.65	0	0	4.45	1.67	4.18	3.56
	1.46	4.77	0	0	4.45	1.78	4.26	3.62
	1.46	4.88	0	0	4.45	1.90	4.34	3.71
20								

The Table 21 data generally show a Ca/Zn molar ratio of 2 or greater, and as the molar ratio of total halides to zinc increases, the pH of the solution increases, as is desired to decrease the thermal decomposition of the biopolymers and common fluid loss control materials normally added to brines used in drilling. Figure 11 presents the data from the last two columns in Table 21: pH is plotted versus the logarithm of the molar ratio of total halides to

zinc. The logical justification of the form of the plot in Figure 11 can be seen from considering Equation 4, which defines the function  $pZn - pX$ :

$$pZn - pX = \log \left[ \frac{\text{Total Halides}}{\text{Zn}} \right] \quad (4)$$

Since pH is  $-\log[H^+]$ , a function of similar form to  $pZn - pX$ , it makes sense to plot pH as the vertical axis in Figure 11. The horizontal axis in Figure 11,  $\log \{$   
 5       $(\text{Total Moles } X^-)$   
 $/(\text{Moles Zn})\}$ , is actually  $pZn - pX$ . Surprisingly, over three quarters of the data cluster about the straight line shown in Figure 11 in the vicinity ranging from pH 2 to about pH 4.5. Then the pH breaks over and appears to level off around pH 5.1 to 5.5. The transition occurs around  $\log\{X^-/\text{Zn}^{2+}\} = pZn - pX = \log\{6\}$ , i. e., around  $X^-/\text{Zn}^{2+} = 6$ . This ratio is consistent with an interpretation that a stable zinc complex anion stoichiometry,  $\text{ZnX}_6^{4-}$ , has been reached in this vicinity; and low pH forms like  $\text{Zn(OH)}\text{X}_5^{4-}$  have been minimized or even largely eliminated, as indicated in Reaction 5, and its variants, below:



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**EXAMPLE SEVENTEEN****USES OF INVENTIVE DENSE, VISCOSEIFIED  
AQUEOUS COMPOSITIONS**

Inventive compositions find advantageous use as replacements for conventional drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids, these uses being well known in the art to which the invention pertains.

**What is claimed is:**

1. A dense, viscosified, aqueous composition finding advantageous use as subterranean drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids, and having superior stability under stress factors such as aging, heat, mechanical agitation and shear, comprising:
  - 5 water;
  - a water-soluble or water-dispersable polymer capable of viscosifying an aqueous medium;
  - 10 one or more cations including a member selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, zinc, or mixtures thereof; and
  - 15 one or more anions including a member selected from the group consisting of chloride, bromide, iodide, formate, nitrate, acetate, cyanate, thiocyanate, a zinc complex anion or mixtures thereof;
  - wherein there are present either at least two cations or at least two anions; the composition having a property selected from the group consisting of a  $\tau_{50}$  of at least about 1; a  $\psi_{50}$  of at most about 1; a  $\phi$  of at least about 1; a  $\zeta_{50}$  of at least about 1; or a  $\omega_{50}$  of at least about 1.
- 20 2. The composition of claim 1, wherein said polymer is a biopolymer.
3. The composition of claim 1, wherein said polymer is selected from the group consisting of algin; anionic cellulose; anionic polysaccharide; cationic polysaccharide; carboxymethyl cellulose; carboxymethyl hydroxyethyl cellulose; gellan gum; guar gum; gum ghatti; gum karaya; gum tragacanth; gum

arabic; gum acacia; locust bean gum; methacrylic acid polymer; polyamine; polyanionic cellulose; iota, lambda or kappa sulfated polysaccharides; polysaccharides modified by i) cross-linking, ii) hydroxyethylation, iii) hydroxypropylation, iv) carboxymethyl-hydroxyethylation, v) carboxymethyl-hydroxypropylation, vi)carboxymethylation, or vii) carboxylation; rhamsan gum; vinyl compound polymer; wellan gum or glycol-compatible wellan gum; xanthan or xanthan gum; or mixtures of said polymers.

4. The composition of claim 1, wherein the composition comprises from about 0.01 to about 45.0 percent polymer by weight; from about 10.0 to about 90.0 percent water by weight; from about 0.05 to about 85.0 weight percent of a first salt; and from about 0.05 to about 85.0 weight percent of a second salt.
5. The composition of claim 1, wherein the composition comprises from about 0.5 to about 10 percent polymer by weight; from about 10.0 to about 90.0 percent water by weight; from about 2 to about 80 weight percent of a first salt; and from about 2 to about 40 weight percent of a second salt.
6. The composition of claim 1, wherein at least one of said cations is held as a complex having cationic, neutral, or anionic form.
7. The composition of claim 1, comprising a chloride anion and a bromide anion.
- 20 8. The composition of claim 1, comprising a first cation having a +2 charge; a second cation having a +2 charge; and a third cation having a +1 charge.

9. The composition of claim 1, comprising a first cation having a +2 charge; a second cation which is held as a complex having cationic, neutral, or anionic form; and a third cation having a +1 charge.
10. The composition of claim 1, comprising calcium cations, chloride anions and bromide anions.  
5
11. The composition of claim 10, wherein the chloride to bromide ratio is from about 20/80 to about 80/20.
12. The composition of claim 10, wherein the chloride to bromide ratio is from about 30/70 to about 60/40.
- 10 13. The composition of claim 1, comprising calcium cations and zinc cations.
14. The composition of claim 1, comprising calcium cations and a zinc complex.
15. The composition of claim 1, comprising zinc cations and a zinc complex.
16. The composition of claim 1, comprising sodium cations, calcium cations and zinc cations.  
15
17. The composition of claim 1, comprising sodium cations, calcium cations and a zinc complex.
18. A method for making a high-density, viscosified, aqueous composition finding advantageous use as subterranean drilling, drill-in, completion,

hydraulic fracturing, work-over, packer, well treating, testing, spacer, or hole abandonment fluids, and having superior stability under stress factors such as aging, heat, mechanical agitation and shear, comprising:

providing an aqueous solution prepared by dissolving into water a  
5 first amount of a first salt and a second amount of a second salt; and  
mixing a water-soluble or water-dispersible polymer into the solution  
to yield a viscosified composition; wherein the viscosified composition has a  
property selected from the group consisting of a  $\tau_{50}$  of at least about 1; a  $\psi_{50}$  of  
at most about 1; a  $\phi$  of at least about 1; a  $\zeta_{50}$  of at least about 1; or a  $\omega_{50}$  of at  
10 least about 1.

19. The method of claim 18, the solution having a density of at least about 9.5 pounds per gallon.

20. The method of claim 18, the solution having a density of at least about 10 pounds per gallon.

15 21. The method of claim 18, the solution having a density of at least about 11.5 pounds per gallon.

22. The product obtained by performing the method of claim 18.

23. In a method for performing hydraulic fracturing, the improvement  
comprising using as the hydraulic fracturing fluid a composition prepared by a  
method comprising:  
20

providing an aqueous solution prepared by dissolving into water a  
first amount of a first salt and a second amount of a second salt; and

mixing a water-soluble or water-dispersible polymer into the solution to yield a viscosified composition; wherein the viscosified composition has a  $\tau_{50}$  of at least about 1.

Viscosity and Temperature vs Time  
14.2 ppg  $\text{CaBr}_2$  + 3 ppb Xanvis  
Fann Model 50 Viscometer

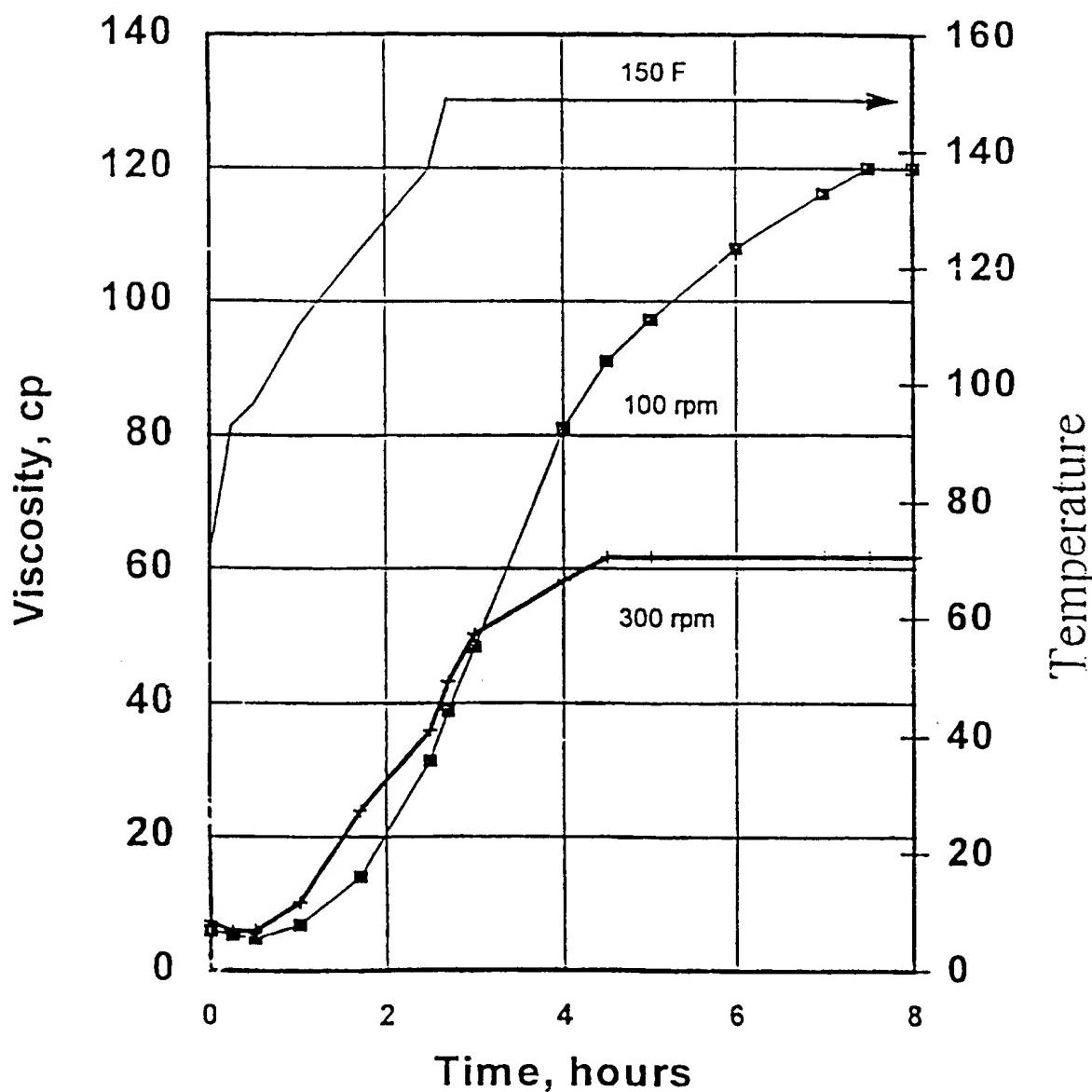
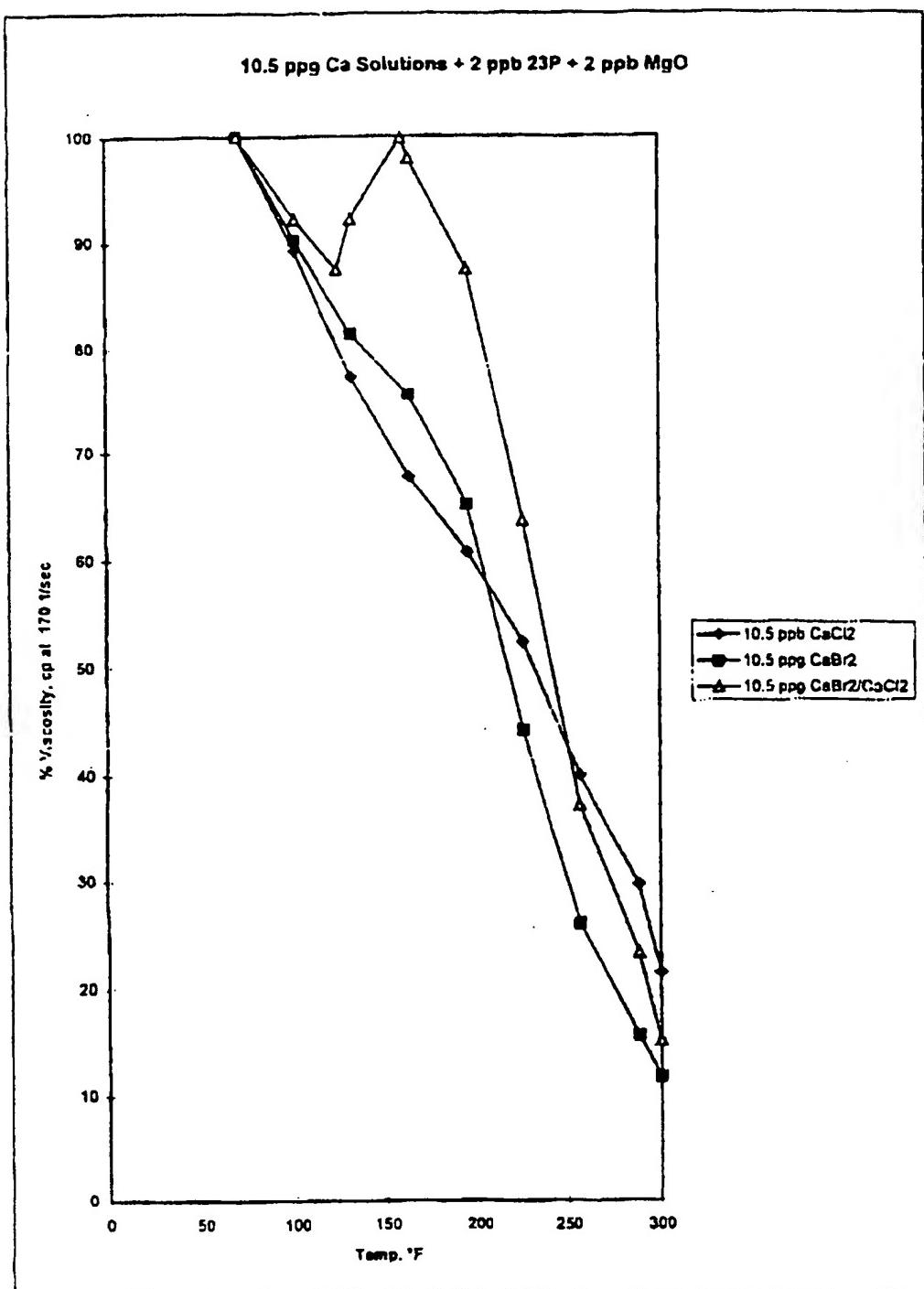


Figure 1

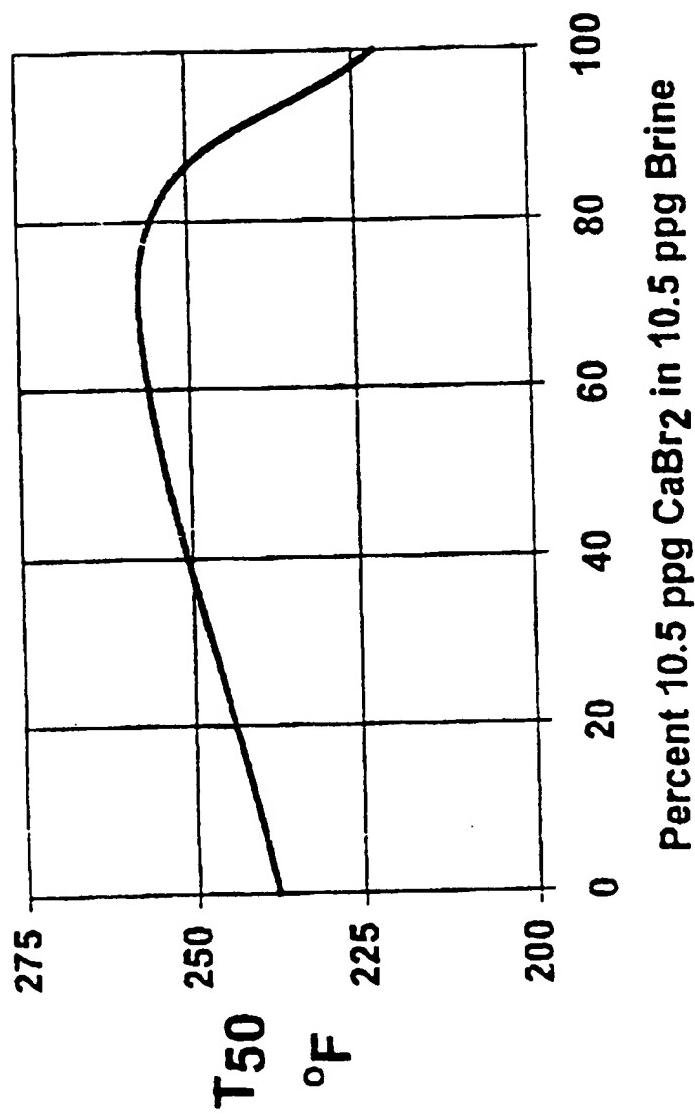
Note: 300 rpm = 511 1/sec & 100 rpm = 170 1/sec  
DV6-47.PPT

2/11

Figure 2

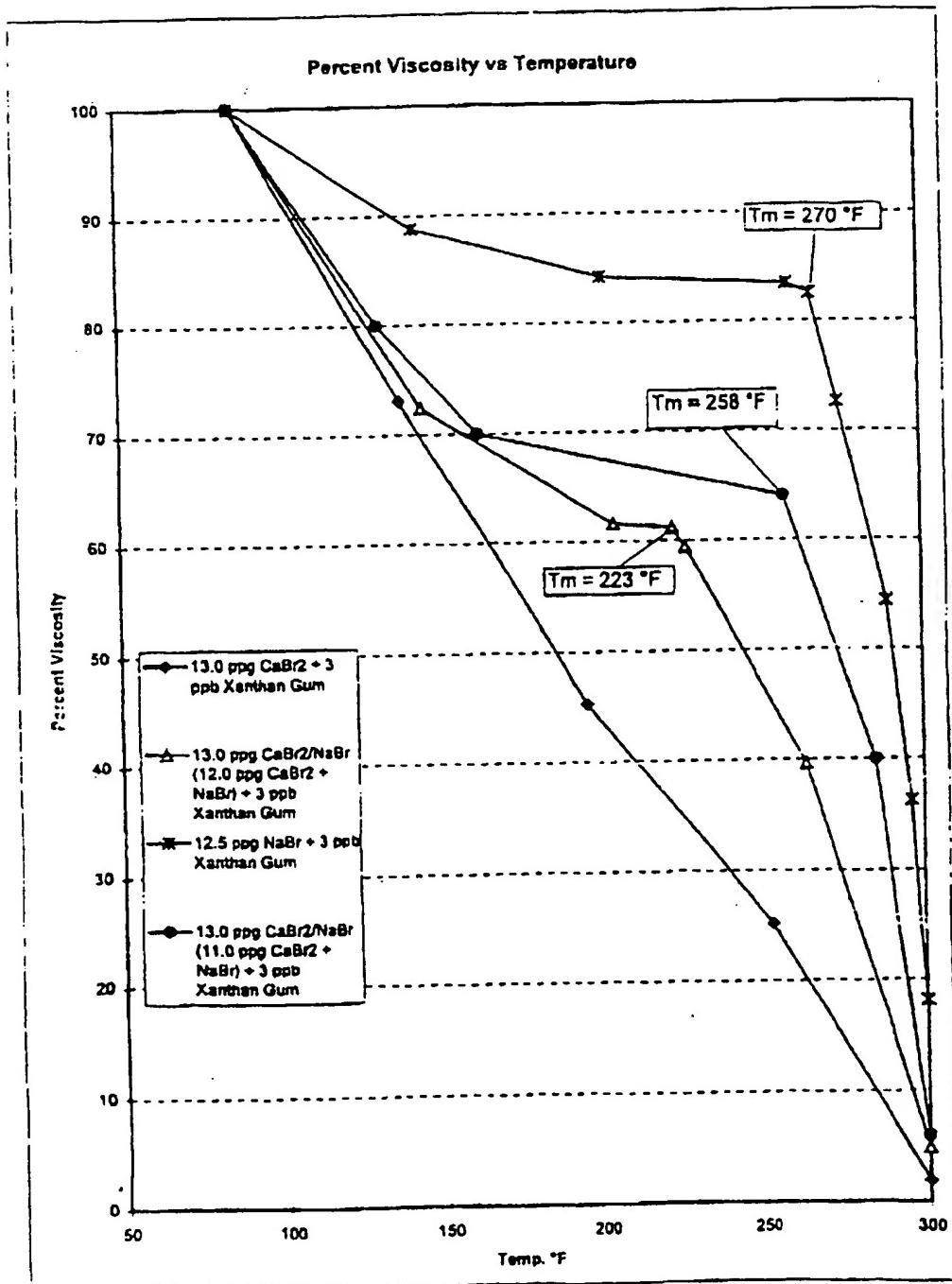


**Figure 3**  
**T<sub>50</sub> VS. %CaBr<sub>2</sub>**  
**10.5 ppg CaCl<sub>2</sub>/CaBr<sub>2</sub> Brines**

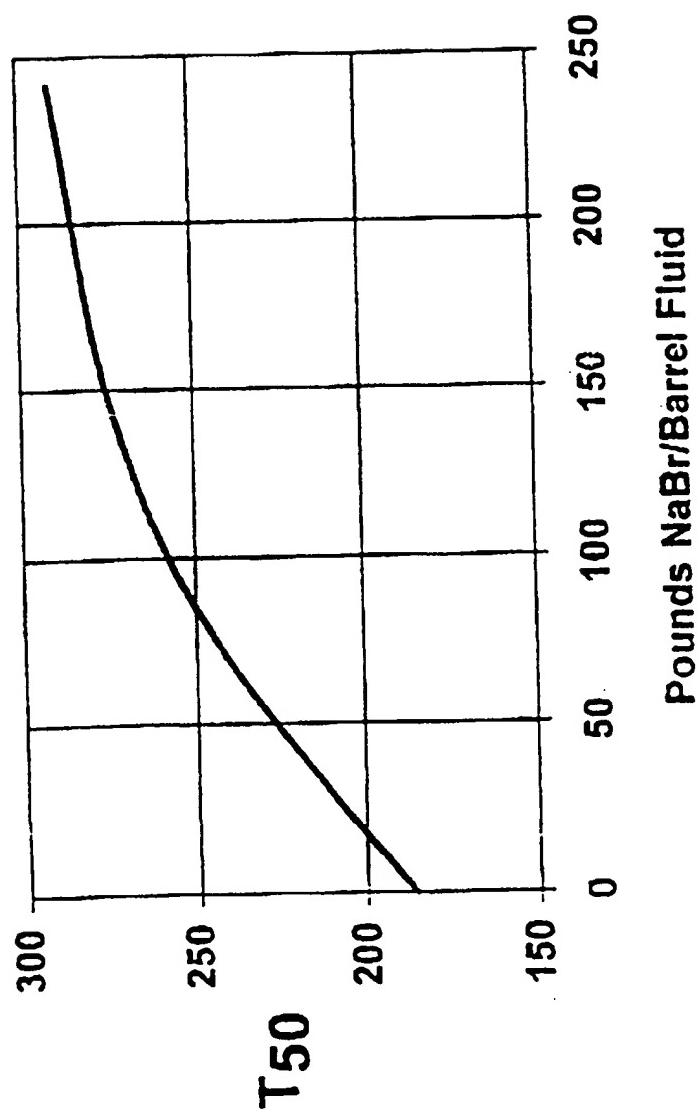


T50-CIBr.PPT

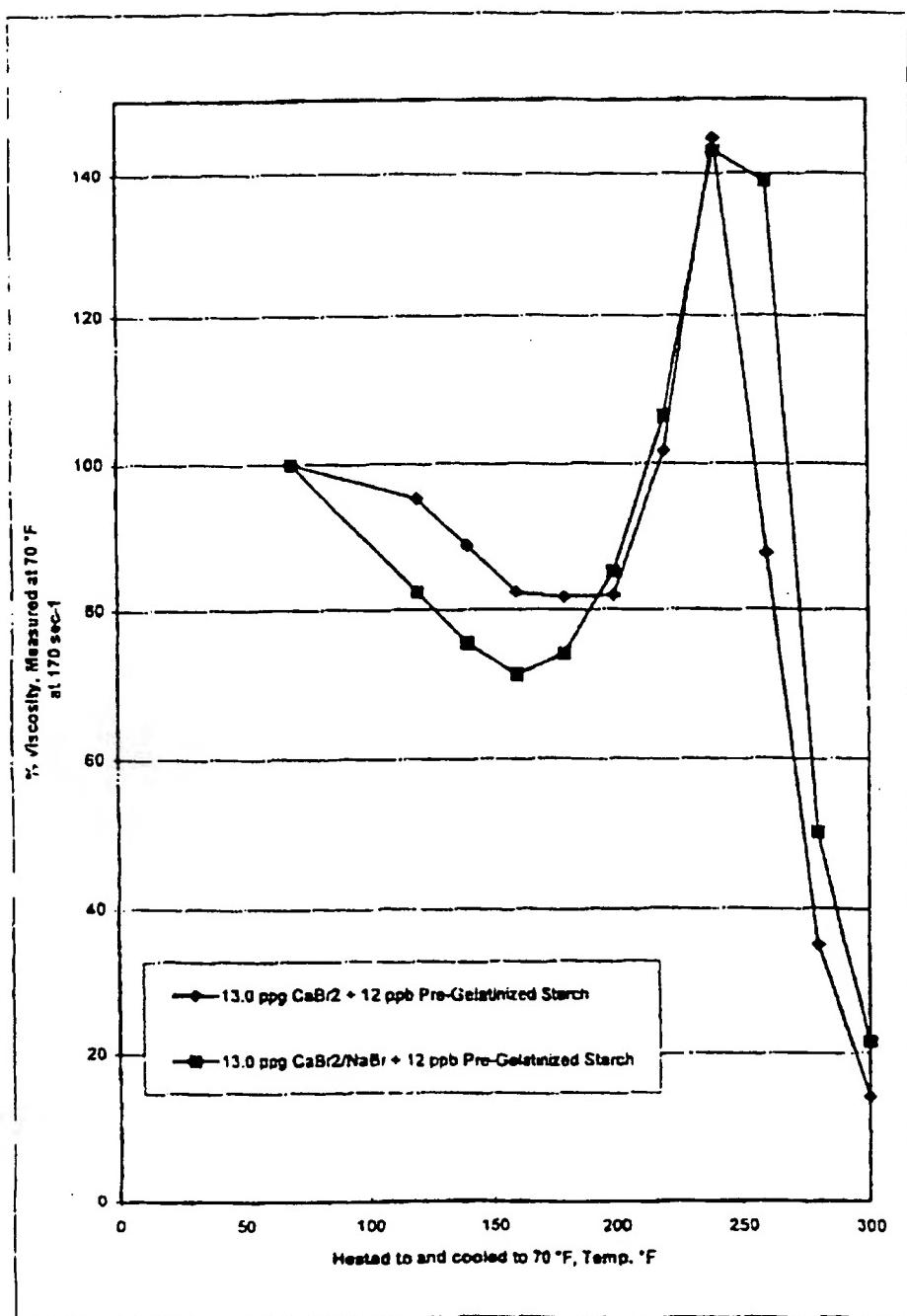
Figure 4



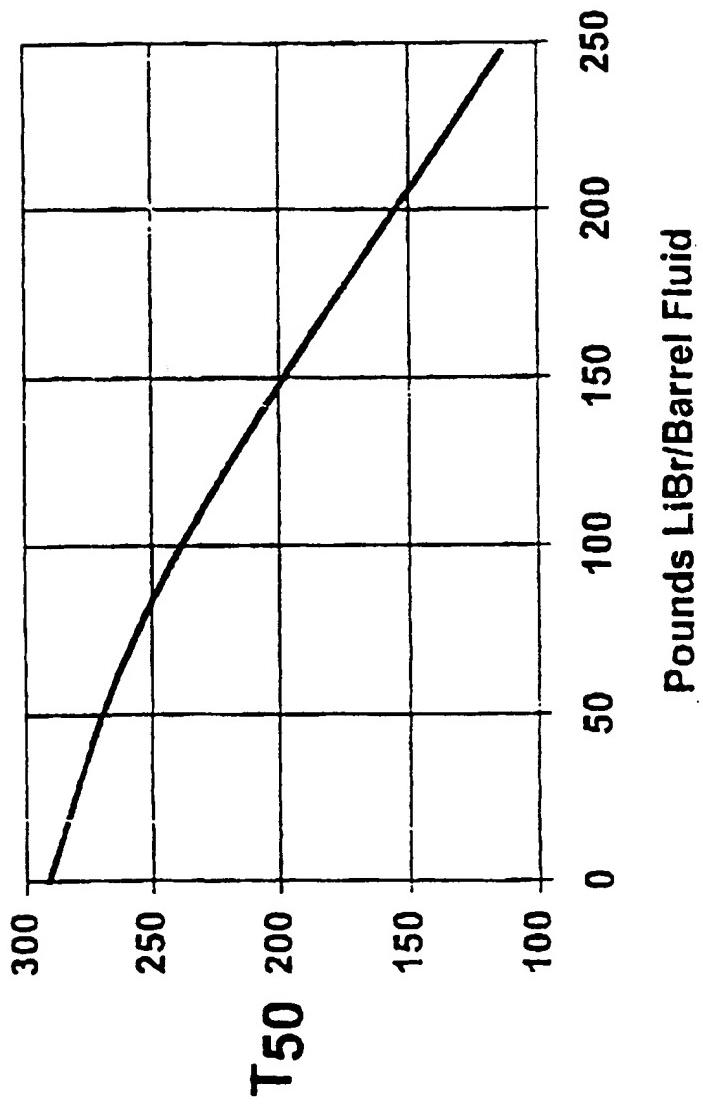
**Figure 5**  
**13 ppg  $\text{CaBr}_2$  /  $\text{NaBr}$  Brine**



T<sub>50</sub>-CaNa,PPT

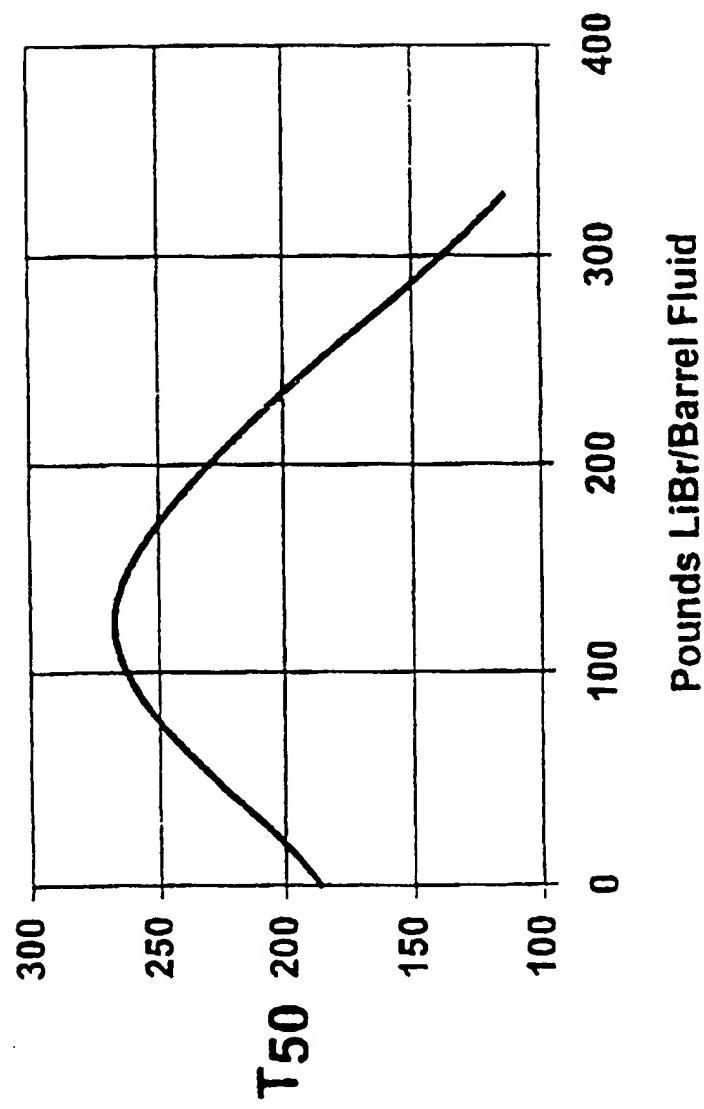
**Figure 6**

**Figure 7**  
**12.5 ppg NaBr / LiBr Brine**

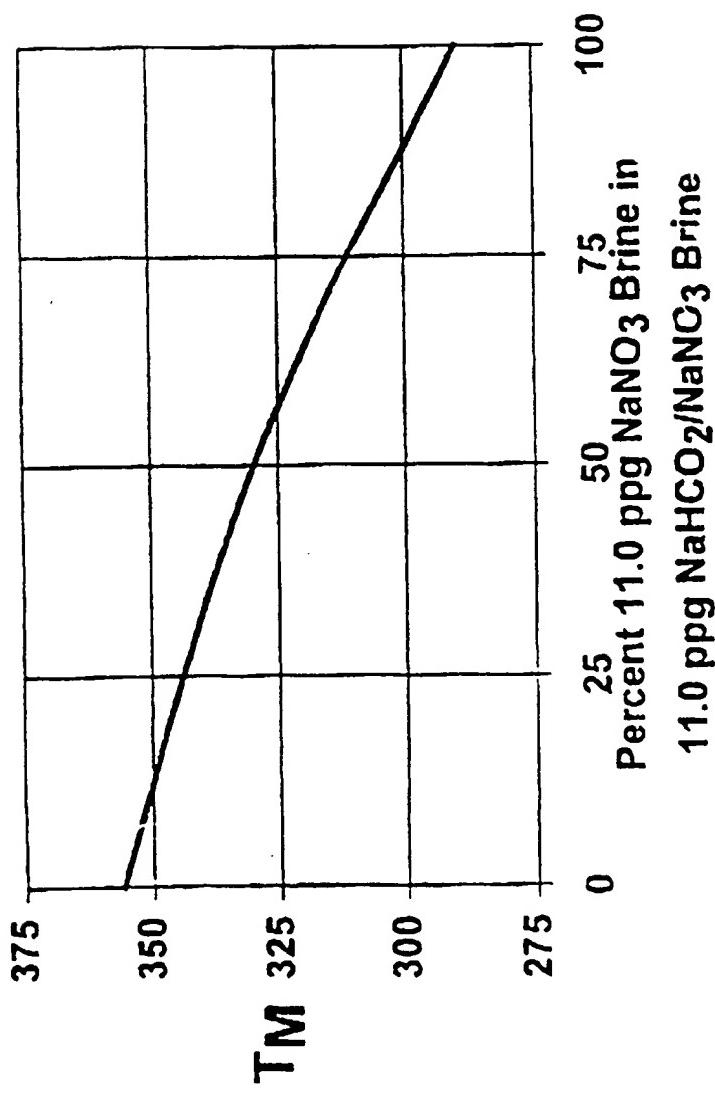


T50-LiNa.PPT

**Figure 8**  
**13 ppg CaBr<sub>2</sub> / LiBr Brine**

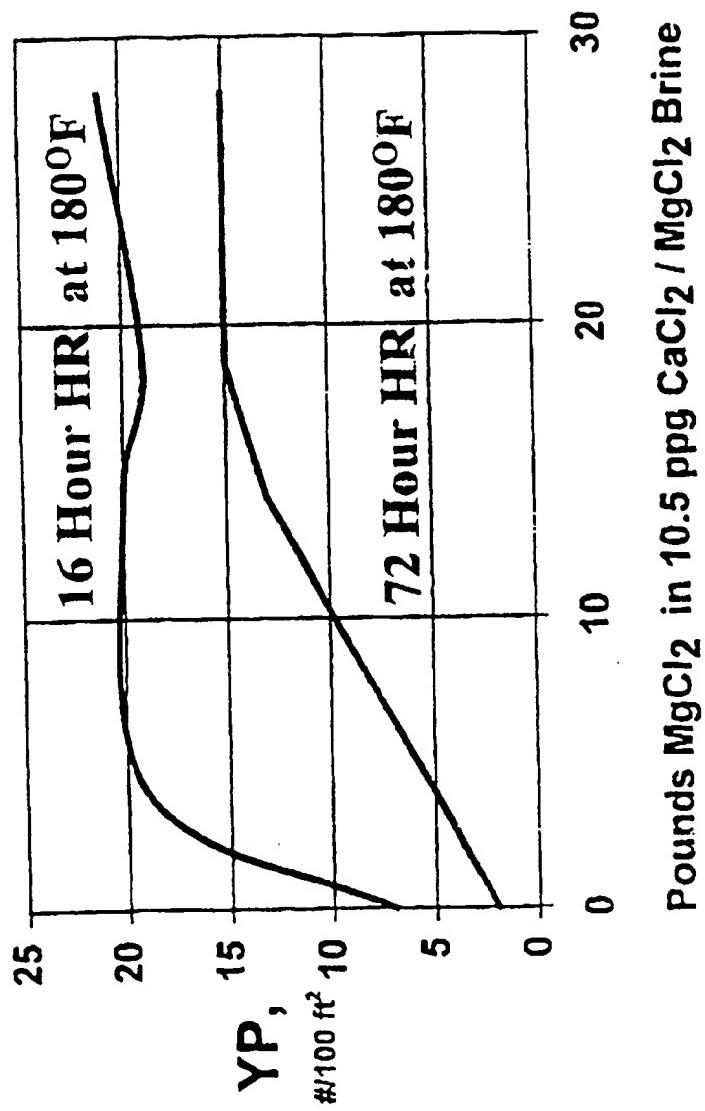


**Figure 9**  
**11.0 ppg NaHCO<sub>2</sub> / NaNO<sub>3</sub> Brine**



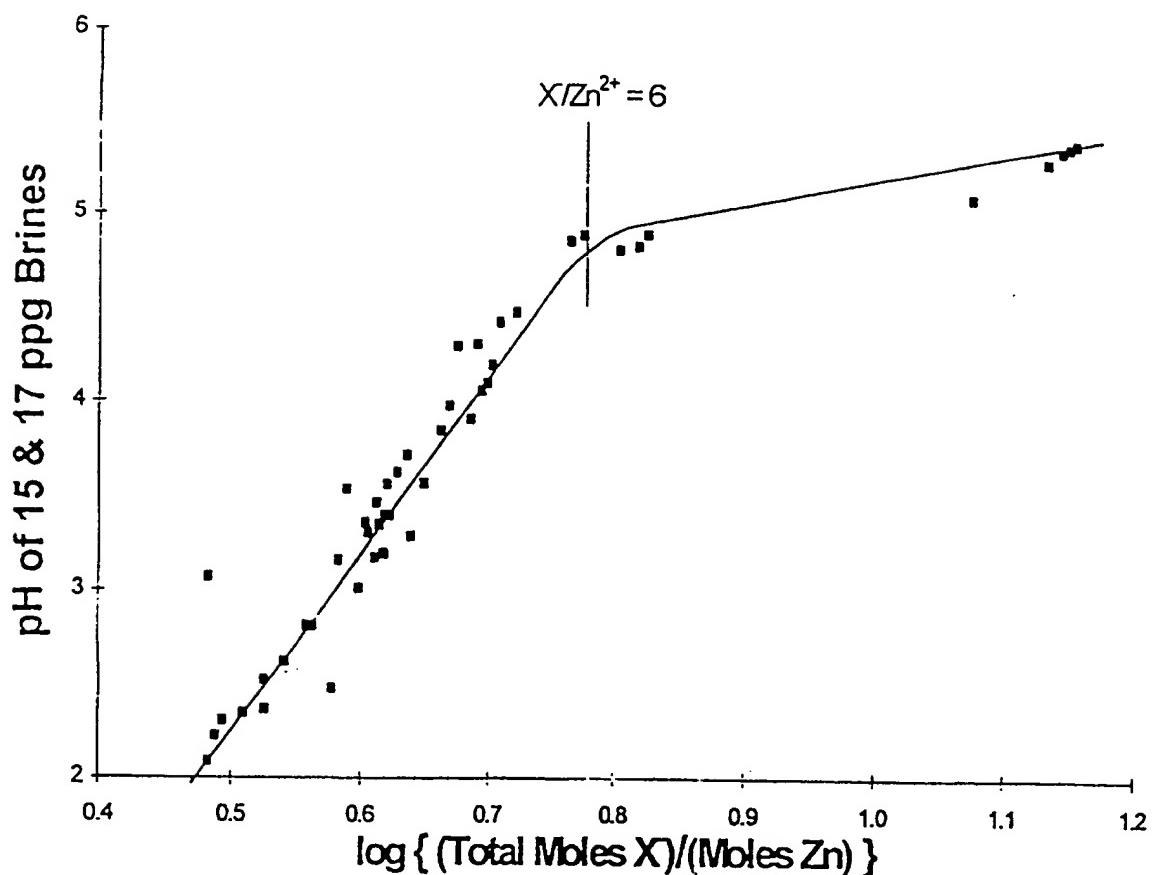
TM-NO3-F.PPT

Figure 10  
10.5 ppg  $\text{CaCl}_2 / \text{MgCl}_2$  Brine



MgCa-YP PPT

Figure 11  
pH vs. Molar Ratio of  
Total Halide to Zinc



## INTERNATIONAL SEARCH REPORT

I. National application No.  
PCT/US97/01176

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 7/02

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 507/110, 111, 112, 113, 114, 140, 141, 145, 209, 211, 212, 213, 214, 215, 216, 269, 272, 276, 277.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,615,740 A (PELEZO et al.) 07 October 1986, see Example 2.	1-7, 10, 13, 14, 18-23
---		-----
Y		11, 12
X	US 5,480,863 A (OAKLEY et al.) 02 January 1996, see Example 1.	1, 4-6, 13, 14, 18-23
X	US 4,619,773 A (HEILWEIL et al.) 28 October 1986, column 4, lines 45-52 and column 6, lines 29-45.	1, 4, 5, 8 ----- 13, 16, 18-23
---		
Y		
X	US 4,941,982 A (DADGAR et al.) 17 July 1990, see claims 1-6, column 15, lines 11-23.	1-5, 8, 9, 16, 18-23

 Further documents are listed in the continuation of Box C.

See patent family annex.

- \* Special categories of cited documents:
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- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*L\* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- \*&\* document member of the same patent family

Date of the actual completion of the international search  
06 MAY 1997Date of mailing of the international search report  
09 JUN 1997Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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Washington, D.C. 20231  
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PHILIP TUCKER  
Telephone No. (703) 308-1235

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US97/01176**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,836,941 A (THOMAS) 06 June 1989, column 4, lines 3-38.	1-5, 13, 18-23
X	US 4,486,317 A (SANDELL) 04 December 1984, see Examples 5 and 11.	1-5, 18-23
Y	US 4,304,677 A (STAUFFER et al.) 08 December 1981, column 2, lines 12-53	1-5, 13, 18-23

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/01176

A. CLASSIFICATION OF SUBJECT MATTER:  
US CL :

507/110, 111, 112, 113, 114, 140, 141, 145, 209, 211, 212, 213, 214, 215, 216, 269, 272, 276, 277.